PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. XVIII. Nos. 245—258.
JANUARY—DECEMBER, 1902.

EDITED BY THE SECRETARIES.

LONDON
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1903.

RICHARD CLAY AND SONS, LIMITED,
BREAD ST. HILL E.C., AND
BUNGAY SUFFOLK

540.6 C42
v.18-20

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£15 to A. W. Crossley, for an investigation of the action of phosphorus haloids on substituted dihydroresorcins under varied conditions.

£10 to F. C. Garrett and J. A. Smythe, for the continuation of an investigation of the bases contained in Scottish shale oil.

£5 to E. P. Perman, for the continuation of an investigation of the partial pressures of ammonia and water vapour in the gases given off by an aqueous ammonia solution.

£10 to K. J. P. Orton, for an investigation of the process of nitration in anilines and in other benzenoid substances.

£5 to J. S. Lumsden, for an investigation of the properties of hexahydro-benzoic, -phenylacetic, and -hydrocinnamic acids.

£10 to J. J. Sudborough, for the continuation of an investigation of the esterification constants of certain organic acids, and of the derivatives of trinitrobenzene.

£10 to A. R. Ling and B. F. Davis, for an investigation of the action of diastase on starch.

£25 to W. J. Pope, for the continuation of his investigation of organo-tin compounds, for the preparation of substances containing asymmetric phosphorus and selenium atoms, and for the general extension of our knowledge of optical activity.

£10 to G. D. Lander, for an investigation of the imino-ethers and allied compounds.

£15 to A. Lapworth, for an investigation of isomeric change and allied phenomena.

£15 to A. McKenzie, for an investigation of fractional esterification and the hydrolysis of isomerides.

£10 to W. H. Mills, for the continuation of an investigation of the synthesis of hydrocarbons.

£20 to R. H. Pickard, for an investigation of the constitution of cholesterol.

£20 to James Walker, for an investigation of tetra-alkylammonium hydroxides.

£20 to A. W. Crossley, for the continuation of his investigation of the action of phosphorus haloids on substituted dihydroxyresorcinols.

£10 to Miss I. Smedley, for an investigation of the colour of iodine-containing compounds.

£20 to A. G. Perkin, for the continuation of his investigation of natural colouring matters.

LIST OF FELLOWS ELECTED DURING 1902.

Name.	Proposed.	Elected.
Alder, John Frederick	November 6th, 1902.	December 4th.
Ashe, James Samuel	March 6th, 1902.	April 30th.
Baker, Frederick G. S.	February 6th, 1902	April 30th.
Ball, James H.	May 15th, 1902	June 18th.
Beanes, Alfred Edward	November 6th, 1902.	December 4th.
Benham, Keith Benham	December 19th, 1901.	February 19th.
Bergtheil, Cyril	February 19th, 1902.	April 30th.
Black, Walter Geoffrey	November 21st, 1901.	February 19th.
Blair, Herbert	November 6th, 1902.	December 4th.
Blenkinsop, Richard	February 6th, 1902.	April 30th.
Boardman, Ernest	February 19th, 1902.	,, ,,
Brincker, John A. H.	November 6th, 1902.	December 4th.
Bruce, Alexander	February 6th, 1902.	April 30th.
Bryant, Vernon Seymour	November 6th, 1902.	December 4th.
Bucknell, Edwin Thomas H.	May 28th, 1902	June 18th.
Burrows, Harry	December 5th, 1901.	February 19th.
Burt, Bryce Chudleigh	May 15th, 1902	June 18th.
Buxy, Tarit Kanti	February 6th, 1902.	February 19th.
Carmichael, Thomas Burnell	November 6th, 1902.	December 4th.
Carrodus, Fred	February 6th, 1902.	April 30th.
Catchpole, Frederick E.	November 21st, 1901.	February 19th.
Challen, Matthew Bradbury	January 16th, 1902.	,, ,,
Chance, Kenneth Macomb	December 5th, 1901.	,, ,,
Claudet, Arthur Crozier	May 15th, 1902	June 18th.
Clifford, William	December 5th, 1901.	February 19th.
Clough, William Thomas	April 17th, 1902	June 18th.
Clowes, George H. A.	March 19th, 1902.	April 30th.
Cockle, Charles	November 6th, 1902.	December 4th.
Cook, Arthur James	March 6th, 1902.	April 30th.
Crocker, James Codrington	February 6th, 1902.	,, ,,
Crookes, Henry	March 19th, 1902.	,, ,,
Daniels, James Ward	November 21st, 1901.	February 19th.
Davis, Charles Benson	February 19th, 1902.	April 30th.
Davis, Frederick	November 21st, 1901.	February 19th.
Davis, Henry Wilson	April 17th, 1902	June 18th.
De la Rue, Evelyn Andros	December 19th, 1901.	February 19th.
Dennis, William	,, ,,	,, ,,
Dixon, John Kemp Smith	December 5th, 1901.	,, ,,
Dobson, Henry Arthur	March 6th, 1902.	April 30th.
Dorée, Charles	November 21st, 1901.	February 19th.
Drought, James Justinian	November 6th, 1902.	December 4th.
Edlin, Edgar Leeder	June 5th, 1902.	December 4th.
Edminson, Sidney Robert	November 19th, 1902.	,, ,,
Edwards, Walter Henry	November 6th, 1902.	,, ,,
Elsden, Alfred Vincent	December 5th, 1901.	February 19th.
Everitt, Walter	March, 19th, 1902.	April 30th.
Eynon, Lewis	December 5th, 1901.	February 19th.

Name.	Proposed.	Elected.
Fasnacht, Eugène A.	November 7th, 1901.	February 19th.
Ferrand, Frederick	December 5th, 1901.	,, ,,
Ferrier, John Oliver	,, ,,	,, ,,
Ferris, Percy J.	April 30th, 1902	June 18th.
Foll, Edgar W.	May 15th, 1902	,, ,,
Francis, Francis E.	May 28th, 1902	,, ,,
Garle, John Longsdon	May 15th, 1902	June 18th.
Gill, J. Arthur	March 19th, 1902	April 30th.
Gow, Alexander	April 30th, 1902	June 18th.
Green, Clarence J.	November 21st, 1901.	February 19th.
Green, George Felix D.	June 5th, 1902.	December 4th.
Griffiths, John T.	March 19th, 1902	April 30th.
Grimwade, Wilfrid Russell	November 6th, 1902.	December 4th.
Gumersall, Edward	,, ,,	,, ,,
Gunn, Gilbert	February 6th, 1902	April 30th.
Haas, Paul	December 19th, 1901.	February 19th.
Hallowell, Thomas B.	April 17th, 1902	June 18th.
Hann, Archie C. O.	April 30th, 1902	,, ,,
Harrison, Walter Ernest	,, ,,	,, ,,
Heaton, Noël	January 16th, 1902	February 19th.
Hennessey, Eugene E.	December 19th, 1901.	,, ,,
Holdcroft, George F.	December 5th, 1901.	,, ,,
Hollingworth, David V.	November 6th, 1902.	December 4th.
Holt, Alfred, jun.	,, ,,	,, ,,
Hopwood, Arthur	February 19th, 1902.	April 30th.
Hosking, Arthur Francis	June 5th, 1902.	December 4th.
Hurtley, W. H.	December 19th, 1901.	February 19th.
Jackson, Clements F. V.	November 6th, 1902.	December 4th.
Jackson, William Brannan	January 16th, 1902	February 19th.
Jardin, David S. Smith	December 19th, 1901.	,, ,,
Jardine, Douglas Kennedy	June 5th, 1902.	December 4th.
Kewley, James	March 6th, 1902.	April 30th.
King, Francis E.	February 6th, 1902	,, ,,
King, Sidney I.	March 19th, 1902	,, ,,
Landau, A. Lionel	February 6th, 1902	April 30th.
Lavelle, Selwyn P. J.	January 16th, 1902	February 19th.
Leader, George H.	May 15th, 1902	June 18th.
Leather, John P.	November 6th, 1902.	December 4th.
Lessner, Charles B.	April 17th, 1902	June 18th.
Lidbury, Frank A.	November 6th, 1902.	December 4th.
Liotard, Ernest	,, ,,	,, ,,
Lockitt, Charles H.	February 6th, 1902	April 30th.
Logan, Thomas S.	November 6th, 1902.	December 4th.
Lucas, Harry	December 19th, 1901.	February 19th.
Ludlam, Ernest B.	November 21st, 1901.	,, ,,
MacCallum, Douglas A.	November 6th, 1902.	December 4th.
Mackenzie, John R.	December 19th, 1901.	February 19th.
Macknight, Alexander	March 6th, 1902	April 30th.
Maitland, William	December 19th, 1901.	February 19th.
Mann, William	November 6th, 1902.	December 4th.
Marsh, John	,, ,,	,, ,,

Name.	Proposed.	Elected.
Martin, Francis	December 19th, 1901.	February 19th.
Martindale, William H.	March 6th, 1902	April 30th.
Mathieson, Robert	March 19th, 1902	,, ,,
Mellor, Joseph W.	November 6th, 1902.	December 4th.
Mence, George A. H.	March 19th, 1902	April 30th.
Millington, John Price	November 6th, 1902.	December 4th.
Molesworth, Francis H.	December 19th, 1901.	February 19th.
Moody, James B.	May 15th, 1902	June 18th.
Moore, Thomas H.	April 17th, 1902	,, ,,
Mukerjee, Beni Madhav	November 19th, 1902.	December 4th.
Mundey, Alfred H.	December 19th, 1901.	February 19th.
O'Connor, Sinnott V.	April 30th, 1902	June 18th.
Ogilvie, Allan	January 16th, 1902	February 19th.
Panisset, Sydney G. S.	November 21st, 1901.	February 19th.
Peck, John W.	March 6th, 1902	April 30th.
Phelps, John	November 6th, 1902.	December 4th.
Phillips, Percy P.	May 15th, 1902	June 18th.
Pollitt, George P.	May 28th, 1902	,, ,,
Powney, William E. F.	May 15th, 1902	,, ,,
Přibram, Richard	November 19th, 1902.	December 4th.
Purtan, Herbert	June 5th, 1902.	June 18th.
Ralph, Stephen J.	April 30th, 1902	June 18th.
Ralphs, Edwin	,, ,,	,, ,,
Ramshaw, Walter	February 6th, 1902	April 30th.
Rây, Prafulla C.	April 17th, 1902	June 18th.
Revis, Cecil	February 6th, 1902	April 30th.
Ricketts, Guy D.	June 18th, 1902.	December 4th.
Roast, Harold J.	May 28th, 1902	June 18th.
Roberts, Jonathan H.	February 19th, 1902.	April 30th.
Ross, George A. P.	November 6th, 1902.	December 4th.
Ross, William C.	November 21st, 1901.	February 19th.
Sampson, John W.	November 6th, 1902.	December 4th.
Scholes, William	February 6th, 1902	April 30th.
Sidgwick, Nevil V.	January 16th, 1902	February 19th.
Simpson, Duncan	November 6th, 1902.	December 4th.
Sindall, Robert W.	,, ,,	,, ,,
Sinnatt, Frank S.	December 5th, 1901.	February 19th
Skertchly, William P.	April 17th, 1902	June 18th.
Smith, Leonard	June 5th, 1902.	December 4th
Smith, Robert E. B.	December 19th, 1901.	February 19th
Smythe, John S.	November 6th, 1902.	December 4th
Southworth, William	December 19th, 1901.	February 19th.
Stanger, William C. S.	May 15th, 1902	June 18th.
Stansfield, Edgar	June 18th, 1902.	December 4th.
Stead, Francis B.	November 21st, 1901.	February 19th.
Stewart, Hector	April 17th, 1902	June 18th.
Sutherst, Walter F.	November 6th, 1902.	December 4th.
Swain, James	January 16th, 1902	February 19th.
Taylor, Thomas	March 19th, 1902	April 30th.
Thomson, George S.	November 6th, 1902.	December 4th.
Tidy, Henry L.	November 6th, 1902.	,, ,,

Name.	Proposed.	Elected.
Tindall, Arthur L. B.	February 6th, 1902...	April 30th.
Trimen, Stephen H.	February 19th, 1902..	,, ,,
Tunnicliffe, William W.	February 19th, 1902..	,, ,,
Turner, Lyon V.	December 5th, 1901..	February 19th.
Wain, William C.	February 19th, 1902..	April 30th.
Wallis, Thomas E.	June 18th, 1902.	December 4th.
Webb, Arthur J.	November 21st, 1901.	February 19th.
Wells, John W.	April 17th, 1902	June 18th.
West, Joseph	April 17th, 1902	,, ,,
Wheeler, Edward J.	May 28th, 1902	,, ,,
White, William C.	November 6th, 1902..	December 4th.
Wilkinson, Edward J.	February 6th, 1902...	April 30th.
Wilson, Lyndon	November 6th, 1902..	December 4th.
Womersley, C. E.	November 21st, 1901.	February 19th.
Wood, Frank S.	March 19th, 1902	April 30th.
Young, Thomas A.	February 6th, 1902 ...	,, ,,

FELLOWS DECEASED.

Name.	Elected.	Died.
Abel, Sir F. A.	March 21st, 1848	September 6th, 1902.
Aikman, C. M.	December 3rd, 1885	November 14th, 1902.
Aquino, T. H.	March 4th, 1897	March 16th, 1902.
Blackett, C. R.	December 18th, 1879	October 18th, 1902.
Forsyth, W. C.	February 2nd, 1888	
Gee, T. E.	November 4th, 1875	June 27th, 1902.
Gladstone, J. H.	December 18th, 1848	October 6th, 1902.
Griffith, G.	June 16th, 1859	May 7th, 1902.
Hummel, J. J.	December 18th, 1879	September 13th, 1902.
Irvine, R	December 7th, 1871	March 20th, 1902.
Jackson, R.	December 6th, 1883	October 21st, 1902.
Macadam, W. I.	April 4th, 1878	June 24th, 1902.
Martindale, W.	April 7th, 1870	February 2nd, 1902.
Moore, Ira	March 6th, 1890	February 28th, 1902.
Moss, John	January 19th, 1871	September 2nd, 1902.
Pechmann, H. von	May 7th, 1896	March 19th, 1902.
Randall, W. B.	April 18th, 1843	March 14th, 1902.
Robbins, John	April 13th, 1872	August 8th, 1902.
Roberts-Austen, Sir W. C.	November 7th, 1866	November 22nd, 1902.
Sim, James	December 3rd, 1885	June 21st, 1902.
Simpson, Maxwell	December 16th, 1850	February 26th, 1902.
Thomas, Andrew	November 17th, 1859	December 9th, 1901.
Truman, E.	December 4th, 1873	October 31st, 1902.
Warmington, E. A.	June 15th, 1893	March 12th, 1902.
Wilson, G. F.	November 19th, 1855	March 28th, 1902.
Wislicenus, Johannes	February 2nd, 1888	December 6th, 1902.
Zingler, M.	April 4th, 1878	September 24th, 1902.

TITLES OF PAPERS COMMUNICATED TO THE SOCIETY DURING 1902.

	Page in Proceedings.	Page in Transactions.
January 16th.		
1. An investigation of the radioactive emanation produced by thorium compounds. I. By E. Rutherford, M.A., D.Sc., and F. Soddy, B.A.	2	321
2. The constitution of hydrocyanic, cyanic, and cyanuric acids. By F. D. Chattaway and J. M. Wadmore	5	191
3. A modification of Zeisel's method for the estimation of methoxyl groups. By J. T. Hewitt and T. S. Moore	8	318
4. A new colour reaction of hydroxylamine. By W. C. Ball, B.A.	9	—
5. On the sensitiveness of a thermoregulator. By A. W. C. Menzies	10	—
6. Myricetin. Part II. By A. G. Perkin	11	203
7. The colouring matters of green ebony. By A. G. Perkin and S. H. C. Briggs	11	210
8. The action of methylene iodide on aryl- and naphthylamines: diarylmethylenediamines, acridines, and naphthacridines. By A. Senier and W. Goodwin	12	280
9 The polymerisation of cyanic acid: cyanuric acid and cyamelide. By A. Senier and T. Walsh	13	290
February 6th.		
10. Conversion of 1-hydroxycamphene into β-halogen derivatives of camphor. By M. O. Forster	25	264
11. The influence of temperature on association in benzene solution and the value of the molecular rise of boiling point for benzene at different temperatures. By W. R. Innes, M.Sc., Ph.D.	26	682
12. The magnetic rotation of ring compounds; camphor, limonene, carvene, pinene and some of their derivatives. By W. H. Perkin, sen., Ph.D., F.R.S.	28	292
13. The transport number of very dilute solutions. By B. D. Steele, B.Sc., and R. B. Denison, B.Sc.	29	456
14. An investigation into the composition of brittle platinum. By W. N. Hartley, D.Sc., F.R.S.	30	—
15. Tetrazoline. Part II. By S. Ruhemann and H. E. Stapleton	30	261
16. The solubilities of the calcium salts of the acids of the acetic acid series. By J. S. Lumsden, D.Sc., Ph.D.	31	350

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17. The equilibrium between a solid and its saturated solution at various temperatures. By J. S. Lumsden, D.Sc., Ph.D.	31	363
18. On the union of hydrogen and chlorine. Part IV. The Draper effect. By J. W. Mellor and W. R. Anderson	32	414
19. Note on the constitution of certain organic nitrates. By C. R. Marshall and J. H. Wigner	32	—
20. Resolution of trimethylhydrindonium hydroxide into its optically active components. By F. S. Kipping	33	275
21. Resolution of methylbenzylacetic acid into its optical isomerides. By F. S. Kipping	33	—
22. *d*-Methylhydrindone. The formation of oximes, hydrazones, and semicarbazones. By F. S. Kipping	34	—
23. Optically active methylbenzylacetic acid. By A. Lapworth and W. H. Lenton	35	—
February 19th.		
24. The union of hydrogen and oxygen. By H. B. Baker	40	400
25. Enzyme action. By A. J. Brown	41	373
26. On the velocity of hydrolysis of starch by diastase with some remarks on enzyme action. By H. T. Brown and T. A. Glendinning	43	388
27. Polymerisation products from diazoacetic ester. By O. Silberrad, Ph.D.	44	598
28. Condensation of phenols with esters of unsaturated acids. Part VII. By S. Ruhemann	45	419
29. The chemical change produced by the immersion of lead in distilled water. By F. Clowes, D.Sc.	46	—
30. The bases contained in Scottish shale oil. Part I. By F. C. Garrett and J. A. Smythe	47	449
31. Note on "liquid nitrogen peroxide as a solvent." By P. F. Frankland, F.R.S., and R. C. Farmer, Ph.D.	47	—
March 6th.		
32. The slow oxidation of methane at low temperatures. By W. A. Bone and R. V. Wheeler	51	535
33. Isomeric additive compounds of dibenzylketone and deoxybenzoin with benzal-*p*-toluidine, *m*-nitrobenzal-aniline, and benzal-*m*-nitraniline. Part III. By F. E. Francis, B.Sc., Ph.D.	53	441
34. Mesoxalic semi-aldehyde. By H. J. H. Fenton, F.R.S., and J. H. Ryffel, B.A., B.Sc.	54	426
35. The action of hydrogen peroxide on carbohydrates in the presence of ferrous salts. III. By R. S. Morrell and J. M. Crofts	55	666
36. *m*-Nitrobenzoylcamphor. By M. O. Forster and Miss F. M. G. Micklethwait	55	406

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37. The Cloëz reaction. By F. D. Chattaway and J. M. Wadmore	56	—
38. The picrimidothiocarbonic esters. By J. C. Crocker, B.A.	57	436
39. Robinin, violaquercetin, myrticolorin and osyritrin. By A. G. Perkin	58	473
40. The nitration of *s*-trihalogen anilines. By K. J. P. Orton	58	490
41. Some *s*-nitrochlorobromoanilines and their derivatives. By K. J. P. Orton	59	495
42. The resolution of pheno-α-aminoheptamethylene into its optical isomerides. Tartrates of pheno-α-amino-heptamethylene and of hydrindamine. By F. S. Kipping and A. E. Hunter	60	574
March 19th.		
43. Nitrogen chlorides containing the propionyl group. By F. D. Chattaway	64	637
44. The constitution of the metallic cyanides as deduced from their synthetic interactions: the constitution of hydrogen cyanide. By J. Wade	65	1596
45. The absorption spectra of metallic nitrates. Part I. By W. N. Hartley, D.Sc., F.R.S.	67	556
46. A method of determining the ratio of distribution of a base between two acids. By H. M. Dawson and F. E. Grant	68	512
47. On the molecular complexity of acetic acid in chloroform solution. By H. M. Dawson	69	521
48. On the existence of polyiodides in nitrobenzene solution. By H. M. Dawson and R. Gawler	69	524
49. Derivatives of α-aminocamphoroxime. By A. Lapworth and A. W. Harvey	70	549
50. Preparation of sulphamide from ammonium amidosulphite. By E. Divers and M. Ogawa	71	504
51. Hypoiodous acid. By R. L. Taylor	72	—
52. Synthesis of imino-ethers. *N*-aryl benzimino-ethers. By G. D. Lander	72	591
53. Nitration of *s*-trihalogenacetanilides. By K. J. P. Orton	73	500
54. Purpurogallin. Preliminary Notice. By A. G. Perkin and A. B. Steven	74	—
55. Quercetagetin. By A. G. Perkin	75	—
April 17th.		
56. Dimercurammonium nitrite and its haloid derivatives. By P. C. Ray	85	644
57. Preparation and properties of 4-*iso*propyldihydroresorcin. A correction. By A. W. Crossley	86	—
58. Oxonium salts of fluoran and its derivatives. By J. T. Hewitt and J. N. Tervet	86	663

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59. Influence of substitution on the reactivity of the aromatic metadiamines. By G. T. Morgan, D.Sc.	87	650
60. The influence of certain acidic oxides on the specific rotations of lactic acid and potassium lactate. By G. G. Henderson and D. Prentice, Ph.D.	88	658
61. The amounts of nitrogen as ammonia and as nitric acid, and of chlorine in the rain-water collected at Rothamsted. A report to the Lawes Trust Committee. By N. H. J. Miller	88	—
62. The amounts of nitrogen, as nitrates, and chlorine in the drainage through uncropped and unmanured land. A report to the Lawes Trust Committee. By N. H. J. Miller	89	—
63. Benzylidenecamphoroxime. By M. O. Forster	90	—
April 30th.		
64. The preparation of absolute alcohol from strong spirit. By S. Young, D.Sc., F.R.S.	104	707
65. On the properties of mixtures of the lower alcohols with water. By S. Young, D.Sc., F.R.S., and Miss E. C. Fortey, B.Sc.	105	717
66. On the properties of mixtures of the lower alcohols with benzene and with benzene and water. By S. Young, D.Sc., F.R.S., and Miss E. C. Fortey, B.Sc.	105	739
67. Fractional distillation as a method of quantitative analysis. By S. Young, D.Sc., F.R.S., and Miss E. C. Fortey, B.Sc.	106	752
68. On the vapour pressures and boiling points of mixed liquids. By S. Young, D.Sc., F.R.S.	107	768
69. The correction of the boiling points of liquids from observed to normal pressure. By S. Young, D.Sc., F.R.S.	108	777
70. Vapour pressures and specific volumes of *iso*propyl *iso*butyrate. By S. Young, D.Sc., F.R.S., and Miss E. C. Fortey, B.Sc.	108	783
71. The preparation of highly substituted nitroaminobenzenes. By K. J. P. Orton	111	806
72. The atomic weight of tellurium. Preliminary notice. By A. Scott	112	—
73. Nitrogen bromides containing the propionyl group. By F. D. Chattaway	113	814
May 15th.		
74. The variation with temperature of the surface-tensions and densities of liquid oxygen, nitrogen, argon, and carbon monoxide. By E. C. C. Baly and F. G. Donnan	115	907
75. Comparison of bromonitrocamphane with bromonitrocamphor. By M. O. Forster	116	865

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76. *aa*-Benzoylnitrocamphor and *aa*-benzoyliodocamphor. By M. O. Forster and E. A. Jenkinson	117	—
77. 2 : 4-Dibromo-5-nitro- and 2 : 4-dibromo-3 : 5-dinitrotoluenes and their behaviour on reduction. By W. A. Davis	118	870
78. Note on the purification of hydrochloric acid from arsenic. By L. T. Thorne, Ph.D., and E. H. Jeffers	118	—
79. The radioactivity of thorium compounds. Part II. The cause and nature of radioactivity. By E. Rutherford and F. Soddy	120	837
80. The radioactivity of uranium. By F. Soddy	121	860
May 28th.		
81. Taxine, the alkaloid of yew. By T. E. Thorpe, C.B., F.R.S., and G. Stubbs	123	874
82. The sampling of soils. By J. W. Leather	125	883
83. Some excessively saline Indian well waters. By J. W. Leather	127	887
84. Nitrobromo-derivatives of fluorescein. By J. T. Hewitt and A. W. G. Woodforde	128	893
85. On phosphorus sesquisulphide and its behaviour with Mitscherlich's test. By E. G. Clayton, F.I.C.	129	—
86. Atomic and molecular heats of fusion. By P. W. Robertson	131	1233
87. The preparation of mixed ketones by heating the mixed calcium salts of organic acids. By E. B. Ludlam	132	1185
88. Isomeric additive products of methyl, ethyl, and propyl benzyl ketones with benzylidene aniline. Part IV. By F. E. Francis and E. B. Ludlam	132	956
89. The influence of solvents on the rotation of optically active compounds. Part III. Influence of benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene on the rotation of ethyl tartrate. By T. S. Patterson	133	1097
90. The influence of solvents on the rotation of optically active compounds. Part IV. Influence of naphthalene on the rotation of ethyl tartrate. By T. S. Patterson	133	1134
June 5th.		
91. The action of ungerminated barley diastase on starch. Part I. By J. L. Baker	134	1177
92. The decomposition of chlorates. Part V. Potassium chlorate in presence of oxides of manganese, and the theory of perchlorate formation. By W. H. Sodeau, B.Sc.	136	1066
93. Studies in the tetrahydronaphthalene series. I. The diazoamino-compounds of *ar*-tetrahydro-*β*-naphthalene. By C. Smith, B.Sc.	137	900

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94. Experiments on phosphorus tetroxide. By C. A. West, B.Sc.	138	923
95. The decomposition of compounds of selenium and tellurium by moulds and its influence on the biological test for arsenic. By O. Rosenheim, Ph.D.	138	—
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R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 22/1/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. No. 245.

January 16th, 1902. Prof. EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

Messrs. Jollyman, Kettle, and J. H. Allworthy were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edwin Bayles Atkinson, Scartho House, Great Grimsby; Matthew Bradbury Challen, Daylesford, Victoria; Noël Heaton, 20, Girdlers Road, West Kensington, W.; William Brannan Jackson, Glengowan, Caldercruix, N.B.; Selwyn Philip James Lavelle, Royston Villa, Ashby Road, Burton-on-Trent; Allan Ogilvie, 19, Market Street, Millom, Cumberland; Nevil Vincent Sidgwick, Lincoln College, Oxford; James Swain, 17, Winsham Street, West Side, Clapham Common, S.W.

DAY AND HOUR OF MEETING.

The Council has decided, on the recommendation of the Committee appointed for the purpose, that for the remainder of the Session the Ordinary Meetings of the Society shall be held at the following times:

	JANUARY.	
Thursday	Jan. 16	at 8.0 p.m.
	FEBRUARY.	
Thursday	Feb. 6	„ 8.0 „
Wednesday	„ 19	„ 5.30 „

	MARCH.	
Thursday	March 6	at 8.0 p.m.
Wednesday	„ 19	„ 5.30 „
	APRIL.	
Thursday	April 17	„ 8.0 „
Wednesday	„ 30	„ 5.30 „
	MAY.	
Thursday	May 15	„ 8.0 „
Wednesday	„ 28	„ 5.30 „
	JUNE.	
Thursday	June 5	„ 8.0 „
Wednesday	„ 18	„ 5.30 „

Annual General Meeting, Wednesday, March 26, at 4.30 p.m.

Of the following papers those marked * were read :

*1. **"An investigation of the radioactive emanation produced by thorium compounds." I. By E. Rutherford, M.A., D.Sc., and F. Soddy, B.A.**

The main questions examined by the authors are (1) Can thoria, the emanating power of which has been largely destroyed by ignition, have this property restored to it by chemical treatment? (2) Is emanating power to be regarded as a specific property of thorium, or is it due to the presence of a foreign material? (3) Does the radioactive emanation itself resemble in chemical nature any known substance?

The electrical methods employed for the measurement of emanating power and radioactivity depend on the universal property of the radiations from substances known as radioactive of ionising or producing charged carriers from the gas through which they pass whereby the gas is rendered capable of conducting a current of electricity. The amount of the current, measured by means of a quadrant electrometer, affords the means of comparing the intensities of radiations, and the method is capable of a degree of precision and rapidity impossible with the better known photographic method. Use was made of the rate of decay of the radiation from the emanation with lapse of time to recognise and distinguish between different types of emanation, and the study of the phenomena is thus rendered qualitative as well as quantitative in character. The means

employed for eliminating the effects of the emanation from the effects of the straight line radiation and *vice versâ* were explained.

The first question is conclusively answered in the affirmative. After solution and reprecipitation, no difference was observed in the emanating powers of thorium compounds prepared from ordinary thoria and thoria de-emanated as completely as possible by intense ignition. The latter process must therefore be regarded as an obliteration of the effect rather than a removal of the cause. The de-emanation of thoria by ignition leaves the straight line radioactivity quite unaffected.

With regard to the second question, the attempts first made to separate from thorium a substance to which the emanating power could be traced were not successful. These included a fractionation of the sulphate and a precipitation of thoria by potassium azoimide according to the method of Dennis. No change in either the emanating power or radioactivity was observed in thoria prepared by these methods. Subsequently, results of a different character were obtained.

It was found that water vapour increases and desiccation decreases the normal value of the emanating power, the extremes varying in the ratio of 2 to 1. Cooling acts powerfully in the opposite direction to increase of temperature. At $-78°$, the emanating power was only one-tenth of the normal, but no permanent alteration in value is produced. The lapse of time in increasing the emanating power of freshly prepared thorium hydroxide is very striking. A maximum value appears to be attained after some days, and this is not much affected by sealing up the substance in glass.

An investigation of the third point, the chemical nature of the emanation itself, showed that this possesses the property of chemical inertness which characterises the members of the argon family. Using in the different cases suitable gases to carry the emanation from the thoria, it was subjected to the action of the following reagents on its way to the testing apparatus: red-hot lead chromate, white-hot platinum, platinum black raised gradually to a white heat, red-hot magnesium, zinc dust, and palladium black. In each case the radioactivity of the gas current was quite unaffected, proving that, not only is the emanation not absorbed by these reagents, but also that its radioactivity is not thereby affected. The possible explanation that the emanation is the manifestation of excited radioactivity on the surrounding atmosphere was shown to be untenable by a crucial experiment. Since the only known gases which would survive in unaltered amount the action of all the reagents employed are the gases of the argon family, the authors conclude that the emanation is allied in properties to the elements of this group.

The emanating power of thorium nitrate, which in the solid state is only 1·8 per cent. of that of thoria, is increased 200 times by

solution in water. It was also found that the emanating power of the carbonate varies enormously with the method of preparation, and specimens of it have been obtained differing in the ratio of 80 to 1, of which the highest possesses four times the value of thoria.

A remarkable observation has been made on the solutions from which thorium has been precipitated with ammonia; although these should be free from thoria, they still possess both emanating power and radioactivity in considerable amounts. This has led to the preparation of substances free from thorium, but possessing radioactivity and emanating power indistinguishable from that of thorium, many hundred, in some cases over a thousand, times as active. The identity extended to the penetration power of the rays for metals and the rate of decay of the emanation. The fact that those processes in which a portion of the emanating material is certainly removed from thorium does not much affect the value of the emanating power of the latter, taken in conjunction with the very great variations which this value suffers in different circumstances and often spontaneously with time, leads to the belief that emanating power is the manifestation of a dynamical change rather than a function of matter in the static condition. In the same way as in chemical reaction, the active mass of a reacting solid appears independent of its quantity, so the rate of the change, of which emanating power is a measure, does not depend solely or even mainly on the quantity of emanating material present. The removal of the latter is consequently not accompanied by corresponding changes in the emanating power. The straight line radioactivity, on the other hand, is apparently unaffected by any of the causes which so profoundly alter the value of the emanating power, and appears much more likely to be additive with regard to mass. The effect of the removal of an intensely radioactive and emanating material from thorium is found, in accordance with this view, to reduce the straight line radioactivity of the thorium very materially. These results show that thorium is partially separated from ThX, the constituent responsible for its activity, and the latter can be obtained free from thorium.

The chemical examination of the thorium-free active substances prepared in the manner described showed the presence of an unknown substance, precipitated from its solutions by sodium phosphate. This the authors regard as merely an accidental impurity. The actual ThX is probably present only in minute quantity, exhibiting the behaviour of being dragged down by precipitates, without reference to its true analytical behaviour.

Another method of separation confirms this view. By evaporation of water with which thoria has been shaken for some time, small deposits are obtained which are often of the order of a thousand fold

more active than the original thoria. The washed sample exhibits a considerable reduction of radioactivity after the process, whilst the character of the radiations as before is identical with the ordinary thorium radiation. A careful chemical examination failed to reveal the presence of any other element besides thorium. The view that the radioactivity and emanating power of thorium is to be ascribed to the presence of a minute amount of a constituent ThX of correspondingly great activity is thus confirmed.

Discussion.

Mr. Vernon Harcourt had previously read two papers by Professor Rutherford in the *Philosophical Magazine* which explained the apparatus used by the authors. The authors' conclusion that the influence upon the conducting power of air or other gas interposed between oppositely electrified surfaces is due, not to an imponderable force radiating from the molecules of thoria, but to the escape in minute quantity of some substance which is mixed with the thoria, and which can be dissolved and precipitated, was of very great interest. He might recall the observations and conclusions of Dr. Russell, who had investigated the photographic effect of the emanation from a number of substances, and had similarly concluded that the results were due, not to such an agent as light or electricity, but to the action of hydrogen peroxide.

*2. "The constitution of hydrocyanic, cyanic, and cyanuric acids." By F. D. Chattaway and J. M. Wadmore.

A study of the behaviour of cyanogen chloride, bromide, and iodide shows that they possess the typical and characteristic properties of compounds in which halogen is attached to nitrogen.

They react, for example, quantitatively with solutions of hydriodic acid, sulphurous acid, and hydrogen sulphide, hydrocyanic acid being in each case reformed, whilst iodine, sulphuric acid, and sulphur respectively are produced.

They must consequently be regarded as imino-derivatives and be represented by the constitutional formulæ,

C:N·Cl C:N·Br C:N·I.

The ease with which the cyanogen halogen compounds can be formed from hydrocyanic acid and its salts and again transformed into them makes it in the highest degree probable that these also have the imino-constitution and must be represented by formulæ such as

C:N·H C:N·K C:N·Ag.

Since the cyanides and cyanogen halogen compounds have the above structure, their relations with cyanic acid and the cyanates point to the probability of the latter also having the *iso*-constitution:

O:C:N·H O:C:N·K O:C:N·Ag.

Cyanuric acid also yields a derivative in which all its hydrogen is replaced by chlorine and which has the composition $C_3O_3N_3Cl_3$. It is formed by the action of chlorine on a solution of potassium cyanurate. It is a white powder, insoluble or soluble only with decomposition in most ordinary solvents, which under the microscope is seen to consist of short prisms, m. p. 245°.

Its behaviour shows that the whole of its chlorine is attached to nitrogen. It liberates chlorine when treated with hydrochloric acid, iodine with hydriodic acid, and oxidises sulphurous to sulphuric acid; it reacts explosively with a strong solution of ammonia, nitrogen being evolved, and also with a solution of hydrogen sulphide, setting free sulphur; cyanuric acid is in each case reformed.

Since cyanurates are readily and completely converted into this trichlorimino-derivative, and the latter in many reactions equally readily and completely again into cyanuric acid, the conclusion is justified that the latter and its derivatives are imino- and not hydroxy-compounds, and assuming the ring structure, they must therefore be represented by the formulæ:

A similar study of the behaviour of cyanuric chloride and bromide shows that in them the halogen is attached to carbon and not to nitrogen.

Discussion.

Professor Dobbie said that in a paper (Hartley, Dobbie, and Lauder, *Trans.*, 1901, 79, 848) on the absorption spectra of cyanogen compounds, it had been pointed out that if cyanuric acid possessed the formula usually assigned to it, it differed from all substances hitherto examined in which carbon and nitrogen atoms were united by alternate double and single bonds in showing no selective absorption. This was the case, however, not only with the derivatives of cyanuric, but also of those of *iso*cyanuric acid, so that if cyanuric acid possessed the imino-structure attributed to it by the authors, there still remained

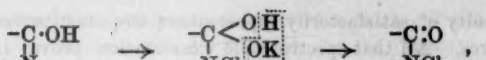
the difficulty of satisfactorily representing the constitution of the *iso*-derivatives. All that spectroscopic examination proves is that it is extremely unlikely that any of these compounds possess a structure analogous to that of pyridine or dimethylpyrazine.

Mr. C. E. Groves said that the very interesting substance, $C_3O_3N_3Cl_3$, to which the authors had given the name of trichloraminocyanuric acid, seemed to have rather the properties of a hypochlorite. Several ring compounds were known somewhat analogous to it in properties, of which the constitutions were accurately known in so far that the chlorine was certainly not attached to nitrogen; such, for instance, was the compound obtained by chlorinating trichloro-orcinol, $C_6Cl_3Me(OH)_2$, which might be represented by the hypochlorite formula, $C_6Cl_3Me(OCl)_2$. If this view were adopted, the formula of the new substance might be represented as $C_3N_3(OCl)_3$, in harmony with that usually assigned to cyanuric acid, $C_3N_3(OH)_3$.

Dr. Lapworth thought that, even if the halogen derivatives referred to had the constitutions which it was proposed to assign to them, it did not follow that the acids from which they are obtained had the same structure. The conclusions drawn were no doubt correct, but this had been decided by physical methods. Reasoning based on the assumption that a substituting atom or group takes up the position originally occupied by the atom displaced could only be accepted with the utmost caution when the molecule is of a labile type.

Thus, in the replacement of the metal in ethyl sodioacetoacetate by alkyls, the new group becomes attached to the carbon atom, but it is not generally conceded that the metal in the original compound occupied that position. Again, by the action of bromine water on phenol, a tetrabromo-substitution product having the structure $O{:}C\langle\begin{matrix}CBr{:}CH\\CBr{:}CH\end{matrix}\rangle C\langle\begin{matrix}Br\\Br\end{matrix}$ is obtained (*Ber.*, 1900, **33**, 674), but this is not a sufficient reason for representing phenol by the formula $O{:}C\langle\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}\rangle CH_2$. In such cases the reactions are open to several interpretations, and in the present case the substitution experiments may be explained equally well by using the alternative formulæ for the acids.

Dr. Forster pointed out that the conversion of cyanuric acid into the chloro-derivative by the action of chlorine on a solution of the acid in potassium hydroxide is an argument which supports the hydroxylic representation of cyanuric acid quite as strongly as the iminic, the change represented by the formula,



leading easily from hydroxylic cyanuric acid to the nitrogen chloride derivative.

Dr. TRAVERS remarked that though the authors had referred to the work of Hartley and others as supporting their theory, the researches of these same investigators on isatin and its methyl derivatives pointed to the danger of accepting such conclusions. Since *ketonic* isatin gives rise, by treating its salts with methyl iodide, to *enolic* methyl isatin, obviously no conclusion could be drawn from such a reaction, which they explain on the basis of the ionic theory.

Professor DUNSTAN was of opinion that in general the tautomerism of these cyanogen derivatives renders it impossible to assign to any one of them a formula which will satisfactorily account for all its reactions. The authors had obtained a very interesting chlorine derivative of cyanuric acid, but its behaviour did not appear to be inconsistent with its being regarded as containing chlorine in the place of the hydrogen of three hydroxyl groups. He considered improbable the authors' explanation of its decomposition by hydrochloric acid giving free chlorine.

Dr. CHATTAWAY in reply said that their work neither proved nor disproved the cyclic constitution of cyanuric acid; it only showed that, whatever the formula, the whole of the hydrogen was attached to nitrogen, and therefore the hydroxylic formula was not possible.

The stability of the chlorine derivative of cyanuric acid and the analogy of its reactions with those of substances such as nitrogen iodide and cyanogen iodide showed that it could not contain –O–Cl groups.

***3. "A modification of Zeisel's method for the estimation of methoxyl groups." By J. T. Hewitt and T. S. Moore.**

The authors described a modification of Zeisel's well-known method in which the condenser supplied with water at 40° is replaced by a fractionating column; this is so efficient that the potash bulbs containing water with red phosphorus in suspension may be dispensed with. The time taken in fitting up the apparatus and in carrying out the operation is much less than in Zeisel's original method. Experimental data were given showing the accuracy attainable.

***4. "A new colour reaction of hydroxylamine." By W. C. Ball, B.A.**

During the course of some experiments on the action of hydroxylamine salts on nickel sulphide, the author obtained an intense purple coloration, which proved eventually to be independent of the presence of nickel or any other metal.

The production of this colour is a very delicate test for hydroxylamine, as solutions so dilute as no longer to reduce Fehling's solution perceptibly, either in the cold or on boiling, easily respond to this test. The best method of applying the reaction is to boil the hydroxylamine solution with one or two drops of yellow ammonium sulphide solution until a precipitate of sulphur is produced; two or three cubic centimetres of 0·880 ammonia solution are then added, and finally an equal volume of strong pure alcohol.

The purple colour thus developed exhibits a characteristic absorption spectrum, consisting of a wide band covering the yellow, orange and part of the green. In stronger solutions, the violet and blue are absorbed, and in very strong solutions the green rays also, so that the only light transmitted is a band in the red.

With a dilution of 1 part of hydroxylamine in 2000 of water the coloration is intense and the band very distinct; with a dilution of 1 part in 300,000 of water, the coloration is still strong, and the band perceptible in 3 centimetres thickness of the solution. By means of this test hydroxylamine may be detected when the dilution does not exceed 1 part in 500,000 of water.

The production of the colour is well adapted for showing the formation of hydroxylamine by the action of metals, for example, tin, on nitric acid. It also serves as a very good means of distinguishing hydroxylamine from hydrazine, as the latter base does not produce the colour. The coloured substance is also produced, and can be obtained in the solid form, by the action of dry ammonia on an alcoholic solution of sulphur monobromide, or an acetone solution of nitrogen sulphide in presence of a little hydrogen sulphide.

The colouring matter seems to be the same as that observed by Fordos and Gélis when nitrogen sulphide containing sulphur is treated with alcoholic potash.

The absorption spectrum of the compound appears to be identical with that of Moissan's sulphammonium, obtained by the action of liquid ammonia on sulphur.

The author is endeavouring to obtain the substance pure enough for analysis.

***5. "On the sensitiveness of a thermoregulator." By A. W. C. Menzies.**

The following details have been recorded, as it is not generally known within what small limits of temperature a bath may be kept constant, using gas heating and the ordinary form of regulator. The glass 'horse-shoe' reservoir was of the usual form, with a capacity of 390 c.c. and an outer surface of about 650 sq. cm.; to this reservoir the ordinary U-form regulating tube which contains mercury, was fused on and the glass connections so bent that all the tubes containing enclosed liquid were under the water of the bath. As toluene was used for the expanding liquid, the stopcock that closes one limb of the U-tube was lubricated with syrupy phosphoric acid. The bath held 14 litres and was of enamelled iron, with no jacket. The stirrer was driven by a small electromotor, and care was taken that a portion of the vibration of the motor was communicated to the regulator, thus aiding the free movement of the mercury in response to the pressure of the toluene. The gas supply to the bye-pass was adjusted by a screw-clip in such a way that the bye-pass flame alone was nearly sufficient to maintain the temperature. Using a tube of 3·1 mm. bore for the outer limb of the regulator, the temperature of the bath can be kept constant at 18° within a total range of 0·008°, that is, 0·004° on each side of the middle point. After 24 days, using unfiltered coal-gas, the actual temperature was the same as at starting, and the closeness of regulation was found still within the above limits. If narrower tubes be used, it is well to dry and filter the gas. The inlet tube that leads the gas down to the surface of the mercury is cut off square and should be so wide that on trial the mercury rises higher in it than in the space between it and the regulator tube. A bore of 1·9 mm. for the outer limb of the regulator gave a temperature variation in the bath of not more (though probably less) than 0·0025 (total range). The difference of temperature between bath and room was 6—7°; if the flame were removed, the bath was found to cool 0·1° in 4·5 minutes. With this regulator, a well-tapped calorimetric thermometer by Golaz, divided into fiftieths of a degree, remained apparently stationary to an estimated tenth-division, as also did a "Beckmann" thermometer graduated directly to hundredths. The limits actually registered by two large special alcohol thermometers (one with a bulb of extremely thin glass 180 mm. long and 5 mm. in diameter) were less than those stated above, which are given after making due allowance for the sluggishness of action of such thermometers.

6. "Myricetin. Part II." By A. G. Perkin.

Myricetin (*Trans.*, 1896, 1287), air-dried, has the formula $C_{15}H_{10}O_8,H_2O$, is anhydrous at 160°, and melts about 357°. The compound previously obtained by the action of bromine is *tetrabrom-myricetin*, $C_{15}H_6Br_4O_8$, and is converted by hydriodic acid into myricetin. *Myricetinpentamethyl ether*, $C_{15}H_5O_8(OCH_3)_5$, m. p. 138—139°, forms a *monoacetyl* derivative, $C_{15}H_4O_8(OCH_3)_5(C_2H_2O)$, colourless needles, m. p. 167—170°, and on decomposition gives gallic acid trimethyl ether and phloroglucinol monomethyl ether, the latter identified by its diazobenzene derivative (m. p. 250—252°). *Myricetinhexaethyl ether*, $C_{15}H_4O_2(OEt)_6$ almost colourless needles, m. p. 149—151°, yields gallic acid triethyl ether and a phenol, probably phloroglucinol diethyl ether (azobenzene compound, yellow needles, m. p. 163—165°). Acetylmyricetin melts at 211—212° and not at 204—206° as previously stated.

Myricetrin, air-dried, $C_{21}H_{22}O_{13},H_2O$; at 160°, $C_{21}H_{22}O_{13}$, pale yellow leaflets, m. p. 199—200°; a new glucoside, occurs in the bark of the *Myrica nagi*, and is decomposed by acid into myricetin and rhamnose, $C_{21}H_{22}O_{13} + H_2O = C_{15}H_{10}O_8 + C_6H_{14}O_6$. It closely resembles quercitrin.

7. "The colouring matters of green ebony." By A. G. Perkin and S. H. C. Briggs.

Green ebony is a yellow dyewood, probably *Excoecaria glandulosa* or *Jacaranda ovalifolia*, until recently employed in this country. It contains two crystalline colouring matters, excoecarin and jacarandin, in minute quantity. *Excoecarin*, $C_{13}H_{12}O_5$, yellow needles, m. p. 219—221°, a weak, substantive dyestuff with animal fibres, forms a *tribenzoyl* compound, $C_{13}H_9O_5(C_7H_5O)_3$, colourless needles, m. p. 168—171°, and a *dimethyl* ether, m. p. 117—119°, yellow needles, giving fluorescent solutions. On fusion with alkali, it yields *hydrotoluquinone* ($CH_3:O:O = 1:2:5$), and *hydroquinone carboxylic acid*, the latter apparently derived from the former. Bromine in presence of alcoholic potassium acetate forms *excoecarone*, $C_{13}H_{10}O_5$, copper coloured needles, m. p. about 250°, which on reduction is reconverted into excoecarin. Alcoholic quinone solution gives a similar compound ($C_{19}H_{14}O_7$?), green leaflets, m. p. 190°, which is possibly a quinhydrone derivative. *Jacarandin*, $C_{14}H_{12}O_5$, yellow plates, m. p. 243—245°, resembles luteolin in dyeing property, and gives a *diacetyl*, $C_{14}H_{10}O_5(C_2H_2O)_2$, yellow needles, m. p. 192—194°, and a *dibenzoyl* derivative, $C_{14}H_{10}O_5(C_7H_5O)_2$, yellow prismatic needles, m. p. 167—169°. With alcoholic potassium acetate the *salt*, $C_{28}H_{23}O_{10}K$, yellow needles, results, and on fusion with alkali an acid, apparently derived from catechol, is formed. The wood contains

also two orange coloured resins, one of which is a yellow dyestuff, but the other is devoid of tinctorial property.

8. "The action of methylene iodide on aryl- and naphthyl-amines: diarylmethylenediamines, acridines, and naphthacridines." By A. Senier and W. Goodwin.

The compounds obtained by the interaction of methylene iodide and arylamines (*Trans.*, 1901, **72**, 254) were believed to be arylmethylenediamines. The study of these compounds now proves that in the case of the reaction with aniline, the toluidines, and xylidine, such diamines are formed. With ψ-cumidine, however, the well-defined, beautiful, yellow, crystalline compound which results is shown to be a condensation product. Its analysis, vapour density, the fluorescence of its solutions, and the analogy of its formation to the anthracene synthesis of Friedel and Crafts (*Ann. Phys.*, 1887, [vi], **11**, 263) and the acridine synthesis of Bernthsen and Bender (*Ber.*, 1883, **16**, 1802), indicate it to be an acridine:—hexamethylacridine. This view is confirmed by the exactly parallel behaviour of both α- and β-naphthylamine with methylene iodide, giving rise to similar compounds, and the identity of the β-compound with the β-naphthacridine already known. This naphthacridine was discovered by Reed, using a different reaction (*J. pr. Chem.*, [ii], 1886, **34**, 160; 1887, **35**, 298), and has led to interesting results in the hands of Morgan (*Trans.*, 1898, **73**, 536).

The further study of the properties and constitution of hexamethylacridine and α-naphthacridine is being proceeded with and is reserved for a future communication.

The following compounds were described: *Diphenylmethylenediamine*, $CH_2(NHPh)_2$, dark yellow powder, m. p. 65—67°. *Diphenylmethylenediamine platinichloride*, $(C_{13}H_{14}N_2)H_2PtCl_6$, olive-green powder. *Dicarbanilidodiphenylmethylenediamine*, $CH_2(NPh{\cdot}CO{\cdot}NHPh)$. *Ditolylmethylenediamines*, $CH_2(NHC_6H_4Me)_2$; *o-derivative*, colourless crystals, m. p. 156—157°; *p-derivative*, pale yellow crystals, m. p. 149—150°; *m-derivative*, yellow, amorphous but not definite. *Dixylylmethylenediamine*, $CH_2(NHC_6H_3Me_2)_2$, pale yellow, large foliate crystals, m. p. 127—128°. *Dixylylmethylenediamine platinichloride*, $(C_{17}H_{22}N_2)H_2PtCl_6$, golden-yellow powder. *Dicarbanilidocarbanilidodixylylmethylenediamine*, $CH_2[N(C_6H_3Me_2){\cdot}CO{\cdot}NPh{\cdot}CO{\cdot}NHPh]_2$, yellowish-white substance resembling wax, yielding colourless needles when recrystallised, m. p. 203°.

Hexamethylacridine, $(C_6HMe_3)<\begin{matrix}CH\\ \diagup\diagdown\\ N\end{matrix}>(C_6HMe_3)$, fine yellow needles, m. p. 221—222°, sublimes readily, solutions fluorescent. *Hexamethylacridine picrate*, $(C_{19}H_{21}N)C_6H_2(NO_2)_3OH$, fine, brown, plume-like crys-

tals, m. p. 200—202°. *Dinitrohexamethylacridine*, $C_{19}H_{19}(NO_2)_2N$, yellow powder, m. p. 85—87°. *Tribromohexamethylacridine*, $(C_6BrMe_3)<^{CBr}_{N}>(C_6BrMe_3)$, red. *Hexamethylacridine nitrate*, $(C_{19}H_{21}N)HNO_3$, bright scarlet needles, m. p. 163—164° with decomposition. *Hexamethylacridine platinichloride*, $(C_{19}H_{21}N)_2H_2PtCl_6$, scarlet needles. *Hexamethylacridine aurichloride*, $(C_{19}H_{21}N)HAuCl_4$, yellow powder. *Hexamethylacridine mercurichloride*, $(C_{19}H_{21}N)HgCl_2$, dark red, glistening needles with remarkable yellow lustre. *Hexamethylacridine dichromate*, $(C_{19}H_{21}N)H_2Cr_2O_7$, deep red crystals. The *sulphate*, *hydrochloride*, and *nitrite* were also described, as was *ethyl hexamethylacridinium iodide*.

α-Naphthacridine, $(C_{10}H_6)<^{CH}_{N}>(C_{10}H_6)$, pale yellow crystals, m. p. 17°3, sublimes, solutions fluorescent. *Mononitro-α-naphthacridine*, $C_{21}H_{12}(NO_2)N$, m. p. 105—107°. *α-Naphthacridine platinichloride*, $(C_{21}H_{13}N)_2H_2PtCl_6,2H_2O$. *α-Naphthacridine picrate*, $(C_{21}H_{13}N)C_6H_2(NO_2)_3OH$, scarlet needles, m. p. 176—178°. *β-Naphthacridine*, $(C_{10}H_6)<^{CH}_{N}>(C_{10}H_6)$, yellow needles, m. p. 215·5°, sublimes, solutions fluorescent, identical with β-naphthacridine of Reed. *β-Naphthacridine platinichloride*, $(C_{21}H_3N)_2H_2PtCl_6(H_2O)_2$, yellow powder.

9. "The polymerisation of cyanic acid: cyanuric acid and cyamelide." By A. Senier and T. Walsh.

In the polymerisation of liquid cyanic acid, cyamelide is not the only product. The two isomerides, cyamelide and cyanuric acid, are formed. These may be separated by treatment with water. Pure cyamelide so obtained is soluble in water to the extent of 0·01 per cent. at 15°. The solubility of cyanuric acid at 15° is from 0·145 to 0·16 per cent. Phosphorus pentachloride has no action on cyamelide.

At the next meeting, on Thursday, February 6th, at 8 p.m., the following papers will be read:—

"An investigation into the composition of brittle platinum." By W. N. Hartley, F.R.S.

"Conversion of 1-hydroxycamphene into β-halogen derivatives of camphor." By M. O. Forster.

"Tetrazoline. Part II." By S. Ruhemann and H. E. Stapleton.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Wednesday, February 19, 1902.

Benham, Keith Benham,
Dean's Hill, Stafford.
Student. Research Student in University College Laboratory. Am desirous of obtaining the publications of the Society.

William Ramsay.	F. G. Donnan.
Edward C. Cyril Baly.	Robert W. Gray.
Edgar Neumann.	Morris W. Travers.

Black, Walter Geoffrey,
9, Routh Road, Wandsworth Common, London, S.W.
Student of Chemistry. Studied Chemistry three years at the Central Technical College, obtaining the Diploma of the City and Guilds of London Institute.

Henry E. Armstrong.	William A. Davis.
Gerald T. Moody.	James Moir.

George Harker.

Burrows, Harry,
The Green, Southgate, N.
Chemical Student. A.R.C.Sc. Lond., F.I.C., Ph.D. Heidelberg.

William A. Tilden.	Chapman Jones.
W. Palmer Wynne.	G. T. Morgan.

M. O. Forster.

Catchpole, Frederick Edward,
11, Jerningham Road, New Cross, S.E.
Student of Chemistry. Engaged in Research Work at the Central Technical College. B.Sc. London University.

Henry E. Armstrong.	Edwin C. Jee.
T. Martin Lowry.	James Moir.

William A. Davis.

Challen, Matthew Bradbury,

Daylesford, Victoria, Australia.

Director, Daylesford School of Mines. For about four years Assistant at Bairnsdale School of Mines. For several years (*a*) Assayer (*b*) Chemist in charge of Cyanide Works at Stawell. For past three years, and at present, Director of Daylesford School of Mines. Lecturer in Chemistry, Assaying, Metallurgy, &c.

J. Dennant. H. W. Potts.
A. M. Cameron. H. T. Waller.

C. R. Blackett.

Chance, Kenneth Macomb,

Lawnside, Edgbaston.

Gentleman. Passed Cambridge B.A. degree in Chemistry. Director of the British Cyanides Co., Ltd., Oldbury.

Alexander M. Chance. Sidney Williamson.
Horace W. Crowther. Charles T. Heycock.
H. Wood Smith. *James Dewar.*

Clifford, William,

1, Avondale Rd., Wolverhampton.

Chemist and Manager, Sewage Outfall Works, Wolverhampton. Associate of the Royal College of Science, Dublin, in the Faculty of Manufactures.

W. N. Hartley. W. H. Perkin, jun.
J. Holms Pollok. Gilbert J. Fowler.
Hugh Ramage. *J. F. Thorpe.*

W. T. Lawrence.

Daniels, James Ward,

Westwood, Medomsley, R.S.O., Co. Durham.

Headmaster Westwood Board School, Medomsley. I am a Science Teacher in day and evening schools under S.A. Dept. South Kensington and C.C. Durham. Held Saturday Scholarships for five years at Durham Coll. of Science, Newcastle, and Rutherford Coll. under Dr. Bedson and Messrs. Shaw, Garrett of Coll. of Science, and Mr. Smith of Rutherford Coll. I gained many Adv. certificates under S.K. and Durham Coll., and took 1st. Cl. in Hon. Pract. Chemistry S.K. I am a student of Lond. Univ., and believe the publications of this Society will be helpful.

P. Phillips Bedson. Wm. Lewins.
F. C. Garrett. *Arthur Crabtree.*

Frank R. Dudderidge.

Davis, Frederick,

"Stanley," Whalley, nr. Blackburn, Lancs.

Chemist to the Bingswood Printing Co., Whalley Bridge, nr. Stockport. B.Sc. Vict. (Honrs. Chem.), 1897. Scholar of Vict. University (1897—1898). Associate of Owens College. Tutor in Chemistry, Hulme Hall, Manchester (1897—1898). Chemist to Badische Anilin- & Soda-Fabrik, Ludwigshafen o/Rhine (1898—1901). Student at Owens College (1894—1898).

H. B. Dixon. Wm. A. Bone.
W. H. Perkin, jun. D. L. Chapman.
W. H. Perkin.

Dennis, William,

Ocean Road Pharmacy, South Shields.

Manufacturing and Photographic Chemist. I hold advanced certificates in Mathematics, Theoretical and Practical Chemistry, and being engaged in the manufacture of drugs, &c., am wishful to obtain the Society's publications with a view to keeping in touch with current affairs in Chemistry and Allied Sciences.

Robert McClumpha. *Frank R. Dudderidge.*
James Whittle. *Fredk. Gilderdale.*
Duncan T. Richards. *W. F. Butcher.*
Arthur Payne.

Dixon, John Kemp Smith,

Gothic House, Birstall, nr. Leeds.

Analytical Chemist. Assistant Analyst in the Laboratory of the Yorkshire Wool Combers' Association, Ltd., since July, 1900, under Walter Leach, Esq. Four Sessions (1896—1900) as student (chiefly of Chemistry) at the Yorkshire College, Leeds.

Walter Leach. Julius B. Cohen.
Arthur Smithells. H. M. Dawson.
H. D. Dakin.

Dorée, Charles,

87, Gore Road, London, N.E.

Lecturer in Chemistry, Seafield Park College, Hampshire. Open Natural Science Scholar, Christ Church, Oxford, 1892. B.A., 2nd Class Hons. Chemistry, 1896; M.A. 1901. Inter. B.Sc. London University, 1901—1st Class Hons. Chemistry. Science Master Blackburn Grammar School, 1898—1901.

A. Vernon Harcourt. J. E. Marsh.
D. H. Nagel. P. Elford.
H. P. Stevens.

Elsden, Alfred Vincent,
Storrington, Pulborough, Sussex.
Student of Chemistry at University College, London.

William Ramsay.	Morris W. Travers.
Edward C. Cyril Baly.	Edgar Neumann.
F. G. Donnan.	Robert W. Gray.

Eynon, Lewis,
57, Darenth Road, Stamford Hill, N.
Analytical Chemist and Teacher of Chemistry. Chief Chemist to the London Beetroot Sugar Association. Assistant-Demonstrator of Chemistry at the Birkbeck Institute. Co-author of a paper on "Anhydro-Bases" (*Chem. Soc. Journ.*, Oct., 1900). Associate of the Institute of Chemistry.

Raphael Meldola.	Arthur R. Ling.
John E. Mackenzie.	F. Southerden.
Thomas H. Pope.	John R. Brooke.

B. E. R. Newlands.

Fasnacht, Eugène Arthur,
Clayton Mount, Newton Heath, Manchester.
Technical Chemist. Studied Chemistry at the Owens College, and afterwards under Dr. C. A. Burghardt of Manchester. For the last fifteen years Chemist and Manager to Messrs. C. R. Lindsey and Co., Manufacturing Chemists, Clayton, Manchester.

Joseph Gaskell.	Charles Dreyfus.
Arthur H. Tuer.	*Harry Silvester.*
H. S. Shorthouse.	

Ferrier, John Oliver,
Colombo, Ceylon.
Analyst to Colombo Commercial Co., Ltd., Colombo. Attended Chemistry Classes at Heriot-Watt College, and Agricultural Chemistry at Edinburgh University. Over five years Assistant Chemist to Messrs. J. and J. Cunningham, Ltd., Leith, and one and a half years Chemist to the Christmas Island Phosphate Co., Ltd., on Christmas Island.

Samuel Walker.	J. Gibson.
John S. Ford.	*J. Falconer King.*

William H. Sodeau.

Green, Clarence J., B.Sc.,
24 Dalberg Road, Brixton Church, S.W.
Assistant Chemist in the Government Laboratories, W.C. For

three years Student in Owens College. B.Sc. with 1st Class Honours in Chemistry, Victoria, 1898. One year Research Student at Owens College, one year as Priestley Research Scholar at Mason College, Birmingham. Demonstrator in Chemistry at the Owens College six months.

T. E. Thorpe. W. T. Lawrence.
H. B. Dixon. J. F. Thorpe.
W. H. Perkin, jun. Wm. A. Bone.

Haas, Paul,

11, Westbourne Park Road, London, W.

Demonstrator of Chemistry at St. Thomas's Hospital. Clothworker Scholar, 1897. B.Sc. London. First Class Hons. Chem., 1899. Ph.D. Freiburg ¹/B, 1901.

William Ramsay. Edward C. Cyril Baly.
Arthur W. Crossley. Robert W. Gray.
F. G. Donnan.

Heaton, Noël,

20, Girdlers Road, W. Kensington.

Technical Chemistry and manufacture of colours. B.Sc. London, Honours in Chemistry. Formerly Student and Exhibitioner of University College, London.

William Ramsay. J. Nevill Huntly.
Morris W. Travers. Alex. M. Kellas.
Edward C. Cyril Baly. F. R. Stephens.

Hennesey, Eugene Edwin, B.A., B.Sc.,

Bigods, Dunmow, Essex.

Principal of the Countess of Warwick's Secondary and Agricultural School, Bigods. Late Assistant in the Chemical Laboratory of the Royal College of Science, London. Teacher of Chemistry in Lady Warwick's School. Has worked at: (1) the bromination of benzil; (2) the estimation of small quantities of alcohol in water; (3) the condensation of acetylene by means of sulphuric acid. No published work.

Raphael Meldola. W. Palmer Wynne.
William A. Tilden. G. T. Morgan.
Chapman Jones.

Holdcroft, George Frederick,

253, Oxford Street, Manchester.

Analytical Chemist. Articled pupil for past three years at the Manchester Laboratory under W. Lawrence-Gadd, F.I.C. Have

attended practical Course on Organic Preparations, and a Course of Lectures on Physical Chemistry at Owens College, Manchester.

George J. Allen. *Rowland Williams.*
Harry Bowes. *M. W. Jones.*
Wm. A. Bone.

Hurtley, William Holdsworth,
St. Bartholomew's Hospital, London, E.C.

Demonstrator in Chemistry at St. Bartholomew's Hospital and College. Doctor of Science (in Chemistry) of London University. Engaged in teaching Chemistry and Physics at St. Bartholomew's Hospital. Six years as a Student at the Yorkshire College under Professors Thorpe and Smithells. Have published the following papers: (1) "The Chlorodibromo- and the Dichlorobromo-benzenes" (*Trans.*, Dec., 1901); and with Drs. Chattaway and Orton (2) "Notizen über einige Anilide" (*Ber.*, 22, 1900); (3) "Nitrogen Chlorides derivable from *m*-Chloracetanilide" (*Trans.*, 1900, 800).

T. E. Thorpe. Herbert Ingle.
Arthur Smithells. F. D. Chattaway.
K. J. P. Orton.

Jackson, William Brannan,
Glengowan, Caldercruix, N.B.

Technical Chemist. Teacher in Chemical Technology. Analytical Chemist in Bleach, Print, and Dye Works for seven years. Teacher in Wool Dyeing, Cotton Dyeing, Calico Printing, &c., at the Glasgow Dyeing and Weaving College. Registered Teacher under the City Guilds London Institute in Dyeing, Calico and Linen Bleaching and Printing.

Peter B. Scotland. *George H. Hurst.*
C. F. Seymour Rothwell. *Jas. Grant.*
Jul. Hübner. *L. G. Radcliffe.*

Jardin, David S. Smith,
Rathgar House, Rathgar.

Associate of the Royal College of Science, Dublin. Associate of the Institute of Chemistry. Licentiate of the Pharmaceutical Society of Ireland. Temporarily assisting in the Laboratory of the Royal College of Science, Dublin.

W. N. Hartley. J. Holms Pollok.
W. E. Adeney. Hugh Ramage.
Chas. R. C. Tichborne.

Lavelle, Selwyn Philip James,
Royston Villa, Ashby Road, Burton-on-Trent.

Brewer's Analyst. Studied Chemistry under Dr. Percy Frankland for two years at the Mason College, Birmingham, and passed the term examination, and have since studied the Chemistry of Brewing for six months under Matthews and Lott, Burton-on-Trent, and after that I have been occupied for the past two years as Assistant Chemist at Messrs. Worthington and Co., Ltd., Burton-on-Trent.

Chas. Geo. Matthews. C. O'Sullivan.
W. Taverner. Percy F. Frankland.
Adrian J. Brown.

Lucas, Harry,
1, St. Agnes' Place, Kennington Park, S.E.

Demonstrator in Chemistry at the Metropolitan College of Pharmacy First Prizeman Advanced Practical Chemistry, Cardiff Science and Art Schools, Session 1887—1888. Passed Major Exam. Pharmaceutical Society, Xmas, 1895. For past 5½ years Lecturer in Pharmacy and Demonstrator in Organic and Analytical Chemistry.

W. Watson Will. H. A. D. Jowett.
Peter MacEwan. F. Filmer De Morgan.
F. B. Power. Thomas Tyrer.

Ludlam, Ernest Bowman,
University College, Bristol.

Demonstrator of Chemistry. Honours B.Sc. (Vict.) in Chemistry, and Leblanc Medal, 1900. Subscriber to Journal and Proceedings, and desirous of keeping in touch with advances in Chemistry.

J. Campbell Brown. Charles A. Kohn.
Sydney Young. J. Norman Collie.
W. Collingwood Williams.

Mackenzie, John Ross,
31, Bailey Street, Ton-Pentre, Glam.

Head Brewer, Maltster, and Chemist. Thirteen years' experience as such in Scotland, England, and Wales. Three years' Student of Chemistry under A. Price, B.Sc. (Lond.). Silver Medallist in Brewing, Boston, England. Member of Institute of Brewing, London. Honours Certificates in Brewing, City and Guilds of London Institute. At present Head Brewer to Messrs. D. John & Co., Limited, Pentre, Glam.

Basil P. Wigan. *Edward Haworth.*
W. T. Leeming. *Edward J. Russell.*
J. Jackson. *Laurence Briant.*
Thomas Mackenzie. *Walter Howe.*

Maitland, William, B.Sc.,
236, Brookhill, Sheffield.

Junior Demonstrator of Chemistry, University College, Sheffield. Lately Junior Assistant, Chemical Department, University of Aberdeen. At present Junior Demonstrator, University College, Sheffield. Have been engaged, with Professor Japp, in a research on a new synthesis of carbazoles, a preliminary note of which has appeared in the *Proceedings* of the Chemical Society (June 20th, 1901).

W. Carleton Williams. George Young.
F. R. Japp. Wm. B. Davidson.
T. S. Murray.

Martin, Francis,
64, Samuel St., Woolwich.

First Assistant Analytical Chemist, Messrs Siemens Bros. & Co., Ltd. (Woolwich). Training in Practical and Theoretical Inorganic and Organic Chemistry, also Metallurgy, at the Woolwich Polytechnic. Honours pass and prizes in the former, and certificates in the latter, conducted by Mr. J. B. Farlie, F.C.S., &c. Ten years' experience in a Chemical Laboratory, and position as first assistant for the last two years. Assisting the late Dr. E. Obach, F.I.C., F.C.S., in the preparation of his Cantor Lectures on Gutta Percha (see footnote of reprint, p. 82).

W. F. Eichenauer. Lionel M. Jones.
J. B. Farlie. *Chas. R. Darling.*
Charles T. W. Hirsch.

Molesworth, Francis Hylton,
Turramurra, Sydney, New South Wales.

Analytical Chemist, Lecturer in Chemistry, Govt. Technical College, Sydney. Formerly Student, Owens College, Manchester. Lecturer in Chemistry, Geology, &c., to South Australian Govt., now Lecturer in Chemistry at Government Technical College, Sydney.

L. R. Scammell. G. A. Goyder.
Andrew Thomas. *Alexander Orr.*
J. C. Fraser.

Mundey, Alfred Holley,
17, St. Margaret's Road, Plumstead.

Chemist. Senior Assistant Chemist and Metallurgist, Royal Carriage Department, Royal Arsenal. Assistant Lecturer in Chemistry and Metallurgy, Woolwich Polytechnic. Pupil of Mr. J. B. Farlie, F.C.S., &c., appointed Assistant in 1888, and still working under his direction at Royal Arsenal and Polytechnic.

J. B. Farlie. *W. H. Deering.*
Lionel M. Jones. *T. H. Dodd.*
Chas. R. Darling. *Oliver Trigger.*

Ogilvie, Allan,

19, Market Street, Millom, Cumberland.

Analytical Chemist. I was seven years in the laboratory of Messrs. R. R. Tatlock and Thomson, City Analysts, Glasgow; 6 years as student and assistant, and 1 year in charge of Students' Department. I left there to become Senior Chemist at Millom Iron Works, where I have been employed for the last $2\frac{1}{2}$ years.

R. R. Tatlock. A. Humboldt Sexton.
R. T. Thomson. Horatio Ballantyne.
Jas. D. Dougall.

Panisset, Sydney Glyde Stephen,

7, Jersey Road, Strood, Rochester.

Analytical Chemist. Associate of the City and Guilds of London Institute. Late Assistant to Mr. C. E. Groves (Consulting Chemist to the Thames Conservancy). Chief Chemist at Wickham Cement Works, Rochester.

Charles E. Groves. Henry E. Armstrong.
Herbert F. Stephenson. Gerald T. Moody.
D. B. Butler. R. Meldola.

Ross, William Charles,

27, Pitt Street, Edinburgh.

M.B., Ch.B., D.P.H. One session Edinburgh University, Theoretical and Practical Chemistry. One year devoted to analysis of foods, drugs, and water at Messrs. Tatlock and Readman's Laboratory, Edinburgh.

Alex. Crum Brown. G. H. Gemmell.
Hugh Marshall. *Leonard Dobbin.*
W. Ivison Macadam.

de la Rue, Evelyn Andros,

52, Cadogan Square, London.

A Director of Thos. de la Rue and Co. Late Student of Chemistry at Trinity College, Oxford. B.A. in Chemistry, Second Class in Honour School (June, 1901).

Hugo Müller. A. Vernon Harcourt.
Harold Hartley. D. H. Nagel.
Allan F. Walden.

Sidgwick, Nevil Vincent,

Lincoln College, Oxford.

Fellow and Lecturer in Chemistry. M.A. First Class in Final

Chemical School, 1895. D.Sc. Tübingen, 1901. Dissertation "Ueber Acetondipropionsäure und ihre Derivate."

D. H. Nagel.	A. Vernon Harcourt.
Harold Hartley.	W. H. Mills.
G. W. F. Holroyd.	Allan F. Walden.

Sinnatt, Frank Sturdy,

Glenside, Church Lane, Moston, Manchester.

Assistant Lecturer and Demonstrator in Chemistry at the Municipal School of Technology, Manchester. Completed the three years Chemistry Courses in the above School, and have passed several subjects in the Honours Stage (Board of Education and City Guilds). My reason for wishing to join the Society is to obtain its publications to assist in research work.

William J. Pope.	L. G. Radcliffe.
Jas. Grant.	William Dixon.

Daniel McLaren.

Smith, Robert Eley Blake,

93 Upper Richmond Road, Putney, S.W.

At present Research Student at University College, London. B.Sc. (Lond.), A.I.C. I desire to attend the meetings of the Society and to obtain its publications.

William Ramsay.	F. G. Donnan.
Edward C. Cyril Baly.	Edgar Neumann.
Morris W. Travers.	Robert W. Gray.

Southworth, William,

County Council Farm, Hutton, Preston, Lancs.

Assistant Lecturer in Agriculture and Superintendent of experiments to the Lancs. County Council. Three years' training (day classes) in General and Agricultural Chemistry and in General Science, Harris Institute, Preston. Hons. Certif. Science and Art Dept. in Agricultural Chemistry and Analysis. Four years Assistant Lecturer on Agriculture; and Superintendent of Field and Manurial experiments to the above Council.

George McGowan.	C. Gerland.
Frank T. Addyman.	John B. Coppock.

J. A. Gardner.

Stead, Francis Bernard,

Clifton College, Bristol.

Assistant Master Clifton College. Formerly Science Scholar at

King's College, Cambridge, and Science Master at Aldenham School. First Class in Nat. Sci. Tripos, Parts I and II, 1894—1895.

W. H. Shenstone. H. J. H. Fenton.
C. T. Heycock. W. J. Sell.
J. E. Purvis.

Swain, James,

17, Winsham Street, West Side, Clapham Common, S.W.

Teacher of Chemistry. Wish to avail myself of the Library and Publications of the Society. Reading for Final B.Sc. (Lond.).

W. B. Hards. Frank E. Weston.
B. C. Polkinghorne. Robert Steele.
Thos. W. Berry.

Turner, Lyon Viccars,

Crescent Lodge, St. John's, S.E.

Student of Chemistry. Studied Chemistry for 2 years at the Central Technical College, and have since been engaged in Research Work.

Henry E. Armstrong. Gerald T. Moody.
William A. Davis. James Moir.
Arthur Lapworth.

Webb, Arthur James,

21, Hammelton Road, Bromley, Kent.

B.A., Oxford. Exhibitioner in Chemistry at Magdalen College, Oxford. Interest in the Study of Chemistry. Final Honours in Chemistry, Oxford.

Henry A. Miers. V. H. Veley.
Duncan R. Wilson. J. E. Marsh.
W. W. Fisher. H. Brereton Baker.

Womersley, Charles Edward,

Kilpin Hill, near Dewsbury (Yorks).

Teacher of Chemistry under Board of Education. Chemistry, Honours, South Kensington. For three years Assistant Chemistry Master, Organised Science School, Heckmondwike. At present Chemistry Master, Technical School, Cleckheaton.

R. S. Cahill. Arthur Peacock.
James Foulds. T. W. Lockwood.
Arthur Crabtree.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 12/2/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. No. 246.

February 6th, 1902. Dr. ARMSTRONG, Vice-President, in the Chair.

Messrs. E. L. Sherwood and A. G. Aston were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederic Guy Stirling Baker, Marryatts Lodge, Snaresbrook, Essex; Richard Blenkinsop, Garden Wharf, Battersea, S.W.; Alexander Bruce, 10, Portland Terrace, Plumstead, S.E.; Fred Carrodus, Glen Fern Tower, Lansdowne Road, Wimbledon, S.W.; James Codrington Crocker, 2, Flynore Villas, Swansea; Gilbert Gunn, 209, Rochdale Road, Bury, Lancs.; Frank Eustace King, Woodbury, Polworth Road, Streatham, S.W.; A. Lionel Landau, 20, Highbury New Park, N.; Charles Henry Lockitt, 5, Harley Road, S. Hampstead, N.W.; Walter Ramshaw, 5, Fronwen Terrace, Brecon; William Scholes, 151, Ainsworth Road, Radcliffe, Lancs.; Arthur Lea Butler Tindall, 41, Sunnyside Road, Ilford; Edward John Wilkinson, 8, Blenheim Terrace, Leeds; Thomas A. Young, 318, Chetham Hill Road, Manchester; Cecil Revis, 77, King Street, West Hammersmith, W.

Of the following papers, those marked * were read:

***10. "Conversion of 1-hydroxycamphene into β-halogen derivatives of camphor." By M. O. Forster.**

β-Bromocamphor, obtained by the action of bromine on 1-hydroxycamphene (*Proc.*, 1901, 17, 245), yields camphor when reduced with

zinc dust and acetic acid, and is hydrolysed by alcoholic potash, forming α-campholenic acid. The oxime remains indifferent to alcoholic potash, and is not converted into a nitrile under the influence of mineral acids; it yields a *benzoyl* derivative which crystallises from alcohol in silky needles melting at 71—73°.

β-Chlorocamphor, $C_{10}H_{15}OCl$, prepared from 1-hydroxycamphene and chlorine in acetic acid containing sodium acetate, crystallises from alcohol in long, slender prisms melting at 132·5°; it has $[\alpha]_D = +39·5°$ in chloroform, and $[\alpha]_D = +40·7°$ in alcohol. The *oxime* is isomorphous with β-bromocamphoroxime, and melts at 134°; the *benzoyl* derivative crystallises in silky needles melting at 86°.

β-Chloro-α-bromocamphor, $C_{10}H_{14}OClBr$, produced by the action of bromine on β-chlorocamphor, crystallises from petroleum in tabular aggregates of white prisms, and melts at 101°; it has $[\alpha]_D = +126·5°$ in chloroform.

The *methyl ether* of 1-hydroxycamphene, $C_{10}H_{15}·OCH_3$, formed when the hydroxy-compound is heated with methyl iodide and dry silver oxide, is a colourless, limpid oil which boils at 193—194°, has sp. gr. 0·9314 at 20°, and $[\alpha]_D = -27·3°$. The *ethyl ether*, $C_{10}H_{15}·OC_2H_5$, resembles the lower homologue, and boils at 203—204°; bromine converts it into β-bromocamphor.

***11. "The influence of temperature on association in benzene solution and the value of the molecular rise of boiling point for benzene at different temperatures." By W. R. Innes, M.Sc., Ph.D.**

The molecular rise of boiling point at different temperatures was determined by introducing phenanthrene, benzophenone, and benzil into benzene, boiling under reduced, atmospheric, and increased pressure. A constant pressure was maintained during each series of experiments at reduced or increased pressure by means of an automatic electrically controlled regulator. The molecular rise of boiling point (τ) was also calculated (a) from the heat of vaporisation by means of van't Hoff's formula, $100\tau = RT^2/L$ (calculated A) and (b) from the rate of change of vapour pressure with temperature by means of the equation $100\tau = Mp\Big/\frac{dp}{dt}$ in which M is the molecular weight of benzene and p the mean pressure (calculated B). The calculated molecular rise and the mean experimental values found for concentrations up to 6/100 gram-molecules per 100 grams benzene are given in Table I:

TABLE I.

Temperature.	54°.	58°.	63°.	73°.	80°.	3°.
Calculated A ...	21·6	22·2	23·0	25·0	26·5	29·5
Calculated B ...	21·05	21·6	22·4	24·25	25·5	27·8
Phenanthrene ...	21·0	—	22·4	23·55	25·25	27·3
Benzophenone ...	20·17	—	21·6	23·0	23·8	26·2
Benzil	—	21·0	—	—	23·3	26·24

The molecular rise calculated from the heat of vaporisation is greater than that calculated from the vapour pressure, the difference increasing with increase of temperature. The values found, using phenanthrene as the dissolved substance, agree very closely with those calculated from the rate of change of vapour pressure. The closely related substances benzophenone and benzil give numbers for the molecular rise which are almost identical. The molecular rise for benzophenone is about 0·8 less than that for phenanthrene at the same temperatures.

Series of determinations were carried out at different temperatures with the abnormal substances benzoic acid, *o*-bromobenzoic acid, *β*-benzil monoxime and dimethyl tartrate. It was found that the dissociation of the complex molecules increased with the temperature between 54° and 80° in every case. Between 80° and 93° there was an apparent decrease of dissociation at all concentrations with benzoic acid and *β*-benzil monoxime; *o*-bromobenzoic acid and dimethyl tartrate were more dissociated at 93° in dilute solutions, but in more concentrated solutions the molecular weights became equal to those at 80° with the former substance and greater with the latter.

The heats of dissociation (Q gram calories) of *β*-benzil monoxime, *o*-bromobenzoic acid and benzoic acid were calculated from the molecular weights at different temperatures and found to be of the same order as those of a number of typical dissociating gases. Table II gives the values calculated; V is the volume in litres occupied by the benzene in which 1 gram-molecule of the substance, calculated as double molecules, is dissolved:

TABLE II.

Substance.	T_1.	T_2.	V.	Q.
β-Benzil monoxime	278	331	13	14600
„	331	353	14	19900
o-Bromobenzoic acid.....	331	353	8·18	7500
„	331	353	12·3	5300
Benzoic acid	336	353	8·18	22800

The heat of dissociation of nitrogen tetroxide is 28900 cal., iodine vapour 28500 cal., acetic acid 20000 cal. and dimethyl ether hydrochloride 8600 cal.

Discussion.

In reply to questions by Dr. Travers, Dr. Innes said that several series of determinations of the molecular rise of boiling point were made; there was very satisfactory agreement in every case. The series with abnormal substances at 93° was not repeated, but the fact that the molecular weight of all four substances was higher than might have been expected seemed to show that the anomalous results at this temperature are not due to ordinary experimental error, whilst from the values obtained for the molecular rise of boiling point it appears that they are not due to a constant error in the method.

*12. "The magnetic rotation of ring compounds; camphor, limonene, carvene, pinene and some of their derivatives." By W. H. Perkin, sen., Ph.D., F.R.S.

The remarkable differences between the magnetic rotations of saturated *closed* chain or ring compounds, such as the derivatives of tri-, tetra-, penta- and hexa-methylene, and the open chain compounds of the aliphatic series, both unsaturated and saturated, were first referred to, the ring compounds having a *much lower* rotation than those which have unsaturated open chains, but the *same* composition; their rotation is also *smaller* than that of the saturated open chain compounds from which they differ in composition by $-H_2$.

On comparing the magnetic rotation of the mono- and di-carboxylic acids and ketones of the closed chain compounds with those of the corresponding saturated open chain aliphatic compounds containing the same number of carbon atoms, considerable discrepancies were observed in the amounts by which they differ from each other, which range from about 0·33 to 0·64, and this want of accord has hitherto been an enigma, but it is now found that this is due to the comparisons having been made between the wrong members of the two series. If tri-, tetra-, penta- and hexa-methylene be taken as the first, second, third and fourth members of the series, as they undoubtedly are, and are compared with the first, second, third and fourth members of the aliphatic series, allowing for the difference of composition, $(CH_2)_3$, these discrepancies disappear. The differences between the rotations of these series are then found to be nearly uniform, and amount to about −0·60 in the mono- and di-carboxylic acids, ketones, and monochloro-derivatives of hexamethylene. In the ring hydrocarbons, this difference is, however, much larger, amounting to about 0·988.

The next point considered was the influence of the double or *bridged ring* formation, in which the ring formation from the open chain compound has taken place twice, and therefore with a loss of four atoms of hydrogen. Camphor is a compound of this class, and it was found in its case that the bridged ring affected the rotation to the extent of $-1{\cdot}290$, or a little more than twice that of the single ring. In borneol, an analogous result was obtained, whilst menthol, which contains only a single ring, gave an amount analogous to the synthetical ring compounds.

Camphene also contains a bridged ring, which is unsaturated, and after allowing for this, it gives a difference of $-1{\cdot}337$, which is not very different from that of camphor. The magnetic rotation of pinene, which is isomeric with camphene but differs from it somewhat in the character of the bridged ring, gave results very similar to those of the latter, but which are a little higher.

In the case of the limonenes, which also are isomeric with camphene but contain only a single unsaturated ring along with the unsaturated group $CH_3 \cdot C(:CH_2)$ outside the ring, the rotations are very different, the value of the single ring formation, allowing for unsaturation, being practically the same as in hexamethylene, $0{\cdot}988$.

The rotations of chlorine and bromine derivatives of camphor and the relationships of nitro- and pseudonitro-camphor and camphoryloxime were considered, as well as the rotation of camphylamine, bornyl chloride or pinene hydrochloride and dipentene dihydrochloride.

The refraction values of borneol and camphor and its derivatives were also given.

***13. "The transport number of very dilute solutions." By B. D. Steele, B.Sc., and R. B. Denison, B.Sc.**

The object of this research was to see if it were possible to obtain by the investigation of sufficiently dilute solutions a value for the transport number for solutions of salts such as calcium chloride, which would result in a constant specific ionic velocity when calculated from different salts of the same cation, thus bringing these salts into line with others, such as potassium chloride, to the ions of which definite specific velocities can be assigned. In order to test this question, it was first necessary to develop a method by means of which the transport number could be determined for very dilute solutions. The method employed is a simple modification of that originally used by Hittorf and lately modified by Noyes; it permits of the electrolysis of a practically unlimited volume of solution being carried out in a vessel of reasonable size.

Measurements have been made for calcium chloride, nitrate and

sulphate, and for potassium chloride, in concentrations of one gram equivalent in 250 litres; and, by combination of the transport numbers found with the conductivity at infinite dilution, identical values are obtained for the velocity of the chlorine ion from solutions of the calcium and potassium salts, and for the calcium ion from solutions of the chloride and nitrate. The velocity of the calcium ion calculated from measurements of calcium sulphate solution is, however, about 3·5 per cent. higher. The transport number of potassium chloride agrees with the best determinations made in solutions up to 1/10 normal, and confirms Kohlrausch's assumption that this remains constant with further dilution.

***14. "An investigation into the composition of brittle platinum." By W. N. Hartley, D.Sc., F.R.S.**

Having had to report upon the composition of brittle platinum in the form of fragments of pins used for dental purposes, their average weight being under 20 milligrams each, a description was given of the method by which the absence of metallic impurities, and also of silicon, was proved spectrographically. The brittle and crystalline character of the metal was shown to be in all probability caused by minute quantities of phosphorus or carbon, and by remelting in a lime crucible under the oxyhydrogen flame its malleability was greatly improved, thus confirming the accuracy of the conclusion arrived at.

The difficulty in deciding beyond question whether there were iron lines in the platinum, or platinum in the iron spectrum, or lines of some impurity common to both metals was pointed out, as showing the importance for practical purposes of determinations of wave-lengths made with the greatest accuracy attainable, particularly in the case of such spectra as these where large numbers of lines are so closely grouped together as to have approximately the same wave-lengths.

15. "Tetrazoline. Part II." By S. Ruhemann and H. E. Stapleton.

The authors find that the action of methyl iodide on tetrazoline is complicated, and they described two of the substances which are formed. One of them crystallises in dark blue needles having the formula $C_3H_9N_4I_3$, and is readily decomposed by water with separation of iodine, whilst the other forms colourless, well-developed crystals, and is an iodide of the formula $C_3H_7N_4I$, which may be transformed into the corresponding chloride and into the platinichloride, $(C_3H_7N_4)_2H_2PtCl_6$. The authors gave reasons for their view that this iodide (or the chloride) is not the salt of methyl tetrazoline; their work, however, is not yet advanced enough to fix the constitution of those two compounds, or to explain the reaction by which they are formed.

16. "The solubilities of the calcium salts of the acids of the acetic acid series." By J. S. Lumsden, D.Sc., Ph.D.

It is well known that many calcium salts diminish in solubility with increase of temperature, and in order to obtain further information on this subject the solubilities of the salts of the acids of the acetic acid series have been carefully determined.

Calcium formate is anhydrous when in contact with its saturated solution and gives a simple ascending curve of solubility. The calcium salts of the other acids of the series contain water of crystallisation and all diminish in solubility with rise of temperature until a minimum point is reached, after which the solubility increases.

Of the salts of the normal acids only calcium acetate changes from one crystalline state to another between 0° and 100°, whilst both calcium *iso*butyrate and calcium *iso*valerate have double curves. With the exception of calcium formate all the salts which have been examined, when in contact with their saturated solutions at 100°, consist of crystals which contain 1 molecule of water.

The salts of the normal acids increase in solubility from formate to acetate and propionate, then decrease quickly with the growth in the number of carbon atoms, the salts of the *iso*-acids being more soluble than those of the corresponding normal acids.

17. "The equilibrium between a solid and its saturated solution at various temperatures." By J. S. Lumsden, D.Sc., Ph.D.

The solubilities of the calcium salts of the acids of the acetic acid series were found to be all represented by curves convex to the temperature axis, indicating at first decrease then increase of solubility.

A curve of this shape is in no way anomalous, for by considering the action of heat on each of the factors which condition the equilibrium in a saturated solution, it is seen to be typically a normal curve.

The factors which produce equilibrium in a saturated solution are: the affinity between solid and solvent, the thermal energy of the solid and the pressure of the dissolved particles. By resolving the solubility curve, which is an exact representation of the resultant of these forces at different temperatures, into component curves representing the forces, the influence of temperature on each can be studied.

When each force varies directly as the temperature, the solubility curve is a straight line; when the rate is different it is a curve convex to the temperature axis.

Some experimenters have given curves of solubility concave to the temperature axis, but examination of several curves of that kind has

shown that they have been produced by the joining of points on two convex curves, so cutting out the transition point.

By estimating the heat of solution at two points on a convex curve where the solubility is the same, it was found that the sensible heat was much less at the higher point. It was also found that the heat of solution at any temperature diminishes with the concentration, and that the direction of the solubility curve indicates the heat of solution in a saturated solution only, being positive on a descending and negative on an ascending curve.

18. "On the union of hydrogen and chlorine. Part IV. The Draper effect." By J. W. Mellor and W. R. Anderson.

The momentary expansion which occurs when a mixture of equal volumes of hydrogen and chlorine is exposed to a flash of light is called, after its discoverer, the Draper effect.

This phenomenon is only produced when luminous rays impinge upon a mixture of approximately equal volumes of hydrogen and chlorine, but not upon chlorine alone, either under reduced or under ordinary pressures, or at temperatures between 15° and 100°. It is not produced when chlorine is mixed with steam, air, nitrogen, carbon dioxide, carbon monoxide, or methane. When the effect reaches a certain magnitude the mixture explodes. Although a few sparks bring about no measurable combination of the mixed gases, the joint effects of a great number of sparks at intervals of half an hour or of one hour is measurable, thus showing that chemical combination takes place during the Draper effect. The amount of combination depends not only upon the number but also upon the intensity of the sparks. The Draper effect appears to be due to some disturbance in the gas which attends chemical combination.

19. "Note on the constitution of certain organic nitrates." By C. R. Marshall and J. H. Wigner.

The authors criticise a theory recently advanced by Vignon and Gerin regarding the constitution of mannitol hexanitrate and allied substances. According to the French chemists, these higher nitrates reduce Fehling's solution strongly, whereas the lower nitrated compounds such as glycerol trinitrate have no reducing action whatever. In order to explain this they state that the terminal $-CH_2 \cdot OH$ group of the higher polyhydric alcohols is converted, during nitration, into a hydrated aldehyde group, $-CH(OH)_2$, which, under the influence of the nitrous acid formed during the reaction, is further changed to a $-CH(OH)ONO$ group. This, by the action of the alkali of the

Fehling's solution, is converted to an aldehyde group which acts as the reducing agent.

Against this view it is urged that the amount of nitrite formed during hydrolysis would vary considerably in the different members of the series, which is shown not to be the case. It is further proved that these compounds possess only a slight reducing action which can be explained on other grounds. The authors see no reason for departing from the view that these substances are nitric acid esters of the various alcohols.

20. "Resolution of trimethylhydrindonium hydroxide into its optically active components." By F. S. Kipping.

In continuing his work on hydrindamine (*Trans.*, 1900, **77**, 861; 1901, **79**, 370, 430, and 442) the author has studied some of the salts of trimethylhydrindonium hydroxide, $C_6H_4<\begin{matrix}CH_2\text{———}CH_2\\CH(NMe_3\cdot OH)\end{matrix}>$, in order to compare their behaviour with that of the salts of the parent base.

dl-Trimethylhydrindonium iodide (*Trans.*, 1900, **77**, 469) interacts with silver *d*-bromocamphorsulphonate, giving dl-*trimethylhydrindonium* d-*bromocamphorsulphonate*, which can be separated into different fractions by crystallisation from a mixture of chloroform and ethyl acetate.

The most sparingly soluble fractions yield d-*trimethylhydrindonium* d-*bromocamphorsulphonate*, $C_{12}H_{18}NO\cdot SO_2\cdot C_{10}H_{14}BrO$; it crystallises in slender needles, melts at 199—200°, and in dilute aqueous solution $[\alpha]_D = +70°$.

d-*Trimethylhydrindonium iodide*, $C_{12}H_{18}NI$, prepared from the preceding salt, crystallises from water in lustrous needles, decomposes at about 190° and is very different from the racemic iodide in most respects; its specific rotation in dilute aqueous solution is $[\alpha]_D = +21{\cdot}9°$.

These results show that hydrindamine and trimethylhydrindonium hydroxide behave very differently towards one and the same acid.

21. "Resolution of methylbenzylacetic acid into its optical isomerides." By F. S. Kipping.

Methylbenzylacetic acid, $C_6H_5\cdot CH_2\cdot CHMe\cdot CO_2H$ (α-methylhydrocinnamic acid), contains an asymmetric carbon group, is easily obtained in large quantities and has recently been used for the

preparation of methylhydrindone (*Proc.*, 1901, 17, 181); in order to obtain an optically active acid chloride for various purposes indicated in the following note, the resolution of the acid was attempted.

Fractional crystallisation of the quinine salt gave the desired result; the salt of the *d*-acid is the more sparingly soluble in most solvents, and, after repeated crystallisation from dilute alcohol and ethyl acetate, is obtained apparently free from its isomeride.

Quinine d-methylbenzylacetate crystallises in prisms, melts at 118—119° and is very readily soluble in warm alcohol, but only sparingly so in boiling water; it has a specific rotation $[\alpha]_D = -113°$ in ethyl alcoholic, and $[\alpha]_D = -76°$ in ethyl acetate, solution.

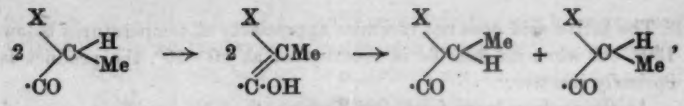
d-Methylbenzylacetic acid is an oil at ordinary temperatures; the highest specific rotation which has been observed with different samples of the acid (without solvent) is $[\alpha]_D = +20{\cdot}3°$. The sodium salt, purified by fractionally precipitating its alcoholic solution with ether, crystallises in colourless plates and has a specific rotation $[\alpha]_D = +26°$ in dilute aqueous solution.

The chloride, prepared by treating the *d*-acid with phosphorus pentachloride and distilling under reduced pressure, is optically active, but probably contains considerable quantities of the *l*-isomeride owing to partial racemisation having occurred.

22. "*d*-Methylhydrindone. The formation of oximes, hydrazones, and semicarbazones." By F. S. Kipping.

When the optically active methylbenzylacetyl chloride described in the preceding note is treated with aluminium chloride under suitable conditions (*Proc.*, 1901, 17, 181) it yields an optically active methylhydrindone, $C_6H_4\langle\begin{matrix}CH_2\\CO\end{matrix}\rangle CHMe$; the specific rotation of the crude product, which is probably a mixture of the *d*- and *l*-isomerides, is about $[\alpha]_D = +25°$ in methyl alcohol.

The optical properties of the ketone seem to undergo no change at the ordinary temperature, so that it consists entirely of the keto-form; in accordance with this conclusion, it does not give a coloration with ferric chloride. When heated at its boiling point under the ordinary pressure for some time the ketone racemises, doubtless owing to keto-enolic isomeric change. It also racemises when treated with small quantities of sodium methoxide, sodium hydroxide, or sodium carbonate in alcoholic solution, and the gradual change in rotation can be followed with the polarimeter. There can be little doubt but that this racemisation is brought about by a keto-enolic transformation.



and these observations afford direct experimental evidence in favour of the accepted views regarding such changes.

Methylhydrindone and hydroxylamine do not seem to interact in absence of alkali, but in presence of potassium hydroxide oxime formation occurs rapidly; the oxime obtained from the *d*-ketone is optically inactive. The *d*-ketone interacts with phenylhydrazine in acetic acid solution, giving a hydrazone; in this reaction also an optically inactive product is obtained. These facts seem to show that oxime and hydrazone formation are preceded by the conversion of the keto- into the enolic form.

When the active ketone is treated with semicarbazide hydrochloride and sodium acetate in aqueous alcoholic solution it yields an optically inactive and an active semicarbazone; the former is probably produced owing to the presence of the *l*-ketone in the original substance, and the formation of an active product seems to show that in semicarbazone formation there is no previous transformation of the keto- into the enolic modification. These and other reactions of ketones are being further investigated.

23. "Optically active methylbenzylacetic acid." By A. Lapworth and W. H. Lenton.

In order to obtain further evidence on the question as to whether α-substitution in acids and ketones is the result of direct replacement of the hydrogen atom or is preceded by the formation of an ethylenic compound with the group $\cdot\dot{C}{:}\dot{C}\cdot O\cdot$, attempts were made to prepare an optically active acid which would undergo racemisation if the latter view were the correct one. For this purpose, methylbenzylacetic acid was thought to be the most convenient substance, as it is easily synthesised and in its usual form is a solid at the ordinary temperature; the quinine salt of the acid was therefore fractionally crystallised from ethyl acetate until the melting point and specific rotation of the least soluble portions remained constant.

Quinine d-*methylbenzylacetate* crystallised from ethyl acetate in well-formed needles which melted at 117°.

d-*Methylbenzylacetic acid*, $CH_2Ph\cdot CHMe\cdot CO_2H$, is a colourless oil; its specific rotation in 1 per cent. ethyl acetate solution was $[\alpha]_D = +14{\cdot}9°$. The *ethyl* ester, under similar conditions, has $[\alpha]_D = +13{\cdot}2°$.

The active acid does not racemise appreciably at temperatures below 130°, but when its chloride is brominated at 80—90°, the product is optically inactive.

As the authors learn from Dr. Kipping that he has been engaged on the study of active derivatives of benzylmethylacetic acid, they propose to leave its further investigation in his hands.

The following additional Candidates have been proposed for election. A ballot will be held on Wednesday, February, 19, 1902, at 5.30 p.m.

Ferrand, Frederick,

13 Torrington St., Hopwood, Heywood.

Works Manager, Heywood, Lancashire. For 17 years Assistant Manager of a wholesale Manufacturing Chemist, Manchester. Now Manager of the Tallow, Oil and Soap Works of Messrs. Hartley and Co., Heywood. A Chemical Research Student.

Evan Williams.	*L. G. Radcliffe.*
Jas. Grant.	*William Dixon.*
Ernest Scott.	*Daniel McLaren.*

The following Certificate has been authorised by the Council under Bye-law I, (3).

Buxy, Tarit Kanti, M.A.,

Jubbulpur, C. P., India.

Professor of Chemistry, Government College, Jubbulpur. Junior Scholar, Entrance Examination, 1890 (Calcutta University) and First in Behar Circle. Senior Scholar, First Arts Examination, 1892, and Second in the University in order of merit. Honours in Mathematics, Physics, and Chemistry in the B.A. in 1894, and Foundation Scholar, Presidency College, Calcutta. Worked in the Presidency College Laboratory under Professors A. Pedler, F.R.S., P. C. Ray, D.Sc. (Edin.), and P. Mukherjee, B.Sc., (Lond.), and stood first in the University in M.A. in Chemistry.

Alex. Pedler.	*Chuni Lal Bose.*
J. Bhaduri.	*H. E. Stapleton.*

ADDITIONS TO THE LIBRARY.

I. By Donation.

Berzelius, J. J. Lehrbuch der Chemie. Aus der schewidischen Handschrift des Verfassers übersetzt von F. Woehler. Vierte Original-Auflage. 1835. 10 vols. From E. W. Prevost.

Church, A. H. Food-grains of India (Supplement). Containing analyses made since the year 1886. Pp. 23. 1901. From the Author.

Gowland, William. The early metallurgy of silver and lead. Part I. Lead. Pp. 64. 1901. From the Author.

Halliburton, W. D. The Croonian lectures on the chemical side of nervous activity. Pp. 99. London 1901. From the Author.

Roscoe, Henry Enfield, and Schorlemmer, C. Ausführliches Lehrbuch der Chemie. 9 vols. Braunschweig 1885—1902. From Sir Henry Roscoe.

Jahresbericht über die Fortschritte der physischen Wissenschaften. Von Jacob Berzelius. Aus dem schwedischen übersetzt von C. G. Gmelin (later) und F. Wöhler. 20 vols. 8vo. Tübingen. 1822—1841.

(Continued under the title):

Jahresbericht über die Fortschritte der Chemie und Mineralogie. Eingereicht an die schwedische Akademie der Wissenschaften. Von Jacob Berzelius. (From 1849—1851. Edited by L. F. Svanberg.) Aus dem schwedischen übersetzt von F. Wöhler. 10 vols. (xxi—xxx). 8vo. Tübingen 1842—1851. Register, i—xxv. 1847. From Sir Henry Roscoe.

Kurzes Lehrbuch der Chemie, nach den neuesten Ansichten der Wissenschaft. Braunschweig 1898. From Sir Henry Roscoe.

Ostwald's Klassiker der exakten Wissenschaften. Photochemische Untersuchungen. 1892. From Sir Henry Roscoe.

Jahresbericht über die Fortschritte der chemischen Technologie für Fabrikanten, Hütten- und Forstleute, Cameralisten, Chemiker und Pharmaceuten. Herausgegeben von Joh. Rud. Wagner. Six vols. 8vo. Leipzig 1855—1860.

(Continued under the title:)

(*a*) Jahresbericht über die Forschritte und Leistungen der chemischen Technologie und technischen Chemie. Herausgegeben von J. R. Wagner. Nine vols. (vii—xv) 8vo. Leipzig 1861—1869.

(Continued under the title:)

(*b*) Jahresbericht über die Foreschritte und Leistungen der chemischen Technologie und technischen Chemie (from vol. xviii) mit besonderer Berüksichtigung der Gewerbsstatistik. Herausgegeben

von J. R. Wagner. Neue Folge. Eleven vols. (xvi—xxvi) 8vo. Leipzig 1870—1880.

(Continued under the title:)

(c) Wagner's (R. von) Jahresbericht über die Leistungen der chemischen Technologie, mit besonderer Berücksichtigung der Gewerbestatistik für das Jahr 1880 (1882). Herausgegeben von F. Fischer. Fourteen vols. (xxvii—xl) 8vo. Leipzig 1881—1894.

II. By Purchase.

Buchka, Karl von. Lehrbuch der Analytischen Chemie. Zweite Auflage. Erster Theil. Leipzig und Wein 1902.

III. Pamphlets.

Boehm, Frederick. Olive oil: its sources, production, character and uses. London 1901. From the Author.

Thwaite, B. H. The generation and transmission of electric energy at and from coal pit centres. Pp. 74. London 1901. From the Author.

Thwaite, B. H. The profitable utilisation of power from blast-furnace gases. Pp. 48. London 1901. From the Author.

Roscoe, H. E. Bunsen. A discourse delivered at the Royal Institution, June 1st, 1900. From the Author.

At the next meeting on **Wednesday, February 19th, at 5.30 p.m.**, there will be a ballot for the election of Fellows, and the following papers will be communicated:

"Enzyme action." By A. J. Brown.

"On the velocity of hydrolysis of starch by diastase, with some remarks on enzyme action." By H. T. Brown and T. A. Glendinning.

"Polymerisation products from diazoacetic ester." By O. Silberrad.

"Condensation of phenols with esters of unsaturated acids. Part VII." By S. Ruhemann and H. E. Stapleton.

"The union of hydrogen and oxygen." By H. B. Baker.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 28/2/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. **No. 247.**

February 19th, 1902. Prof. J. EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

Messrs. E. A. Lewis, R. A. Berry, H. W. Crowther and H. O. Jones were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs:

Bergtheil, Cyril, Checkley, Red Hill, Surrey.
Boardman, Ernest, 41, Knowsley Road, Smithills, Bolton.
Davis, Charles Benson, 218, West 134th Street, New York, U.S.A.
Hopwood, Arthur, 49, Stanley Street, Tunstall.
Roberts, Jonathan Hugh, Oban Gwys, Swansea.
Trimen, Stephen Herbert, 61, St. John's Park, N.
Tunnicliffe, William Wright, Newhall, Burton-on-Trent.
Wain, William Charles, Mercantile Explosive Dept., Sydney, N.S.W.

It was announced that the following changes in the Officers and Council were proposed by the Council:

As Vice-Presidents: Prof. Meldola, F.R.S., and Prof. Frankland, F.R.S., *vice* Mr. Groves, F.R.S., and Prof. Purdie, F.R.S.

As Foreign Secretary; Prof. W. Ramsay, F.R.S., *vice* Prof. Meldola, F.R.S.

As Ordinary Members of Council: Mr. J. E. Marsh, Dr. J. A. Voelcker, Dr. A. Harden, and Dr. Lewkowitsch, *vice* Mr. Fenton, F.R.S., Mr. Howard, Mr. Pope, and Dr. Crossley.

Mr. A. C. Chapman, Dr. Hewitt, and Dr. Thorne were appointed to audit the Society's accounts.

A Ballot for the Election of Fellows was held and the following were subsequently declared duly elected :

Keith Benham Benham.
Walter Geoffrey Black.
Harry Burrows, Ph.D.
T. K. Buxy, M.A.
Frederick E. Catchpole, B.Sc.
Matthew Bradbury Challen.
Kenneth Macomb Chance, B.A.
William Clifford.
James Ward Daniels.
Frederick Davis, B.Sc.
Evelyn Andros De la Rue, B.A.
William Dennis.
John Kemp Smith Dixon.
Charles Dorée, M.A.
Lewis Eynon.
Alfred Vincent Elsden.
Eugéne Arthur Fasnacht.
Frederick Ferrand.
John Oliver Ferrier.
Clarence J. Green, B.Sc.
Paul Haas, B.Sc., Ph.D.
Noël Heaton, B.Sc.
Eugene Edwin Hennessey, B.A., B.Sc.
George Frederick Holdcroft.
W. Holdsworth Hurtly, D.Sc.
William Brannan Jackson.
David S. Smith Jardin.
Selwyn Philip James Lavelle.
Harry Lucas.
Ernest Bowman Ludlam, B.Sc.
John Ross Mackenzie.
William Maitland, B.Sc.
Francis Martin.
Francis Hylton Molesworth.
Alfred Holley Mundey.
Allan Ogilvie.
Sydney Glyde Stephen Panisset.
William Charles Ross.
Nevil Vincent Sidgwick, M.A., D.Sc.
Frank Sturdy Sinnatt.
Robert Eley Blake Smith, B.Sc.
William Southworth.
Francis Bernard Stead, B.A.
James Swain.
Lyon Viccars Turner.
Arthur James Webb, B.A.
Charles Edward Womersley.

Of the following papers, those marked * were read :

***24. "The union of hydrogen and oxygen." By H. B. Baker.**

Experiments have been made during the last ten years by H. B. Dixon, Victor Meyer, and by the author, with the object of seeing if the presence of moisture had any influence on the union of hydrogen and oxygen. These experiments have led to negative results. By the use of a new method of preparing very pure hydrogen and oxygen, namely, by the electrolysis of a solution of very pure barium hydroxide, the author has succeeded in preparing these gases so pure and dry that tubes containing them can be heated to redness without union of the gases, whilst tubes containing the undried gases, heated side by side with the dried tubes, readily explode. On the introduction of a small quantity of distilled water into the dried tubes, explosion follows at once. In gases which had been allowed to stand for two days only in contact with distilled phosphorus pentoxide, only a slow combination took place, so slowly that in one case ten minutes' heating in the flame of a Bunsen

burner caused the union of only one-third of the partially dried gases. It seems therefore that water is not the only determining factor in the explosion of the heated mixture. In order to see if a still higher temperature would bring about the union, coils of very pure silver wire were heated by an electric current in the dried mixture, when it was found that the silver could be heated to its melting point without causing union.

Experiments have also been made with the object of finding out if the moist gases were measurably dissociated whilst the dry gases were not. By a device of Professor Edward Morley's, used for another purpose, gases were sealed up in tubes in which a contraction of less than 1/7000th of their volume could be detected. The gases were dried before their introduction into the tubes by simply passing them through a phosphorus pentoxide tube. They were then left in contact with the pentoxide for six months. No contraction, even to the small extent above noted, could be observed. The gases tested thus were hydrogen, oxygen, nitrogen, air, and a mixture of hydrogen and oxygen. These tubes were kept in a dark room during the whole period.

It was found that a moist mixture of hydrogen and oxygen united slowly in sunlight, which may perhaps account for some previous failures to get the gases dry enough not to unite. In the first series of experiments above described, the mixed gases were kept in darkness during their contact with the phosphorus pentoxide, lest the action of the drying agent should not be sufficiently rapid to cope with the water being produced by their union.

*25. "Enzyme action." By A. J. Brown.

The author has already shown (*Trans.*, 1892, 61, 380) that in alcoholic fermentation a *constant weight* of sugar is decomposed in unit time by a constant amount of yeast in solutions of equal volume containing different amounts of sugar, and has called attention to the fact that in this respect the action of fermentation differs essentially from that of inversion, which, according to C. O'Sullivan and Tompson (*Trans.*, 1890, 57, 865), follows the law of mass action. At the time the author described his work, the phenomenon of fermentation was believed to be a life function inseparable from the living cell, and therefore it did not appear remarkable that the order of progression of its action should differ from that of inversion; but since Buchner has shown that fermentation, like inversion, is an enzyme action, this point of difference required further investigation as the simple mass action of invertase demonstrated by O'Sullivan and Tompson is often regarded as typical of all forms of enzyme action.

The author has examined the action of invertase on cane sugar, and

finds that the velocity of its action differs essentially from that of a mass action, and *resembles that of fermentation.* The velocity of its action represented graphically approximates a *straight line* when not influenced by the accumulation of inversion products. The retarding influence of inversion products occasions the curve found by O'Sullivan and Tompson, and these authors were mistaken in regarding the curve as the logarithmic curve of mass action. In a true mass action the value K, derived from the expression $K = \frac{1}{\theta} \log \frac{1}{1-x}$, for any point of the action is a constant, but this is not the case in inversion changes in which the products of inversion accumulate. On the contrary, for such changes the value $2K$ is nearly constant when derived from the expression, recently suggested by Henri (*Compt. rend.*, 1901, 133, 891), $2K = \frac{1}{\theta} \log \frac{1+x}{1-x}$,—an expression differing essentially from that representing the progress of a mass action.

But although the action of inversion does not follow the law of mass action, it cannot be independent of mass influence, and therefore the effect of mass during inversion change must be restricted by some other influence. This influence the author believes to be due to the existence of time as a factor in the complex changes which probably accompany inversion.

In any simple chemical change the influence of mass regulates the number of molecular *contacts* between acting and reacting molecules in unit time; but if a time factor enters into a molecular reaction there must be a point beyond which the number of molecular *changes* cannot increase owing to the restriction of time in the action, and this point will be determined by the relative frequency of molecular contact and the relative length of the time interval of molecular change. There is good reason to believe that during the inversion of sucrose, this sugar enters into molecular combination with invertase previous to change, which presupposes a complex change and the existence of a time factor of some magnitude. Under these conditions it therefore appears more probable that this factor limits the effect of mass action in inversion changes in solutions of ordinary concentration. But if this is so, there must be a point of dilution in cane sugar solutions when invertase, acting in the dilute solutions, should exhibit an order of change in conformity with simple mass action. The author shows by direct experiment that this point is reached in a solution containing about 1 per cent. of cane sugar, so far confirming the conclusion that a time factor accompanying molecular change limits the action of inversion in all but very dilute solutions of cane sugar.

The action of alcoholic fermentation follows the same order of

progression as that of inversion, and the work of Kastle and Loevenhart (*Amer. Chem. Journ.*, 1900, **24**, 491) indicates that the action of lipase progresses in the same manner,—it therefore appears probable that both these enzyme actions are regulated, like inversion, by a time factor. With regard to the actions of such enzymes as diastase, glucase, and peptase there is not at present sufficient evidence on which to base an opinion.

***26. "On the velocity of hydrolysis of starch by diastase with some remarks on enzyme action." By H. T. Brown and T. A. Glendinning.**

The rate of change during the hydrolysis of starch by diastase does not conform to the simple logarithmic law of a unimolecular reaction. Throughout the hydrolysis there is a steady augmentation of the coefficient of velocity; in other words, within any given time interval there is more of the residual substance hydrolysed than there should be according to the logarithmic formula.

The results are in the wrong direction to be accounted for by a gradual accumulation of the products of change with a consequent tendency to chemical reversion, nor can they be explained by the intermediate products of change exhibiting a differential resistance to hydrolysis.

If the time curves expressing the rate of hydrolysis of a 3 per cent. solution of soluble starch are critically examined, it is found that up to a hydrolysis of 30 to 40 per cent. the amount of transformation is very nearly a linear function of the time. A further analysis of the curve shows that the remainder is approximately logarithmic.

In all essentials, the progress of the hydrolysis of starch coincides with that of the inversion of cane-sugar by invertase, as shown by Adrian Brown in the previous paper. The rate of hydrolysis also conforms closely with the empirical formula of Henri for the inversion of cane sugar.

The authors are inclined to adopt a somewhat different explanation of the time curves of hydrolysis from that suggested by Adrian Brown, and one which does not postulate any difference in the time intervals between the successive stages of the reaction other than those due to variations in the respective masses of the reacting substances existing in unit volume.

This hypothesis has been fully elaborated, and an attempt is also made to link the phenomena of enzyme hydrolysis with those of acid hydrolysis, the water ions, or the active dissociated water molecules, being in both cases regarded as the true hydrolysts.

*27. "Polymerisation products from diazoacetic ester." By O. Silberrad, Ph.D.

In this research, which is a continuation of work already published (Hantzsch and Silberrad, *Ber.*, 1900, **33**, 58), the polymers of diazoacetamide are dealt with. The investigation has led to the discovery of a third series of polymeric products from diazoacetic ester, of which the most stable representative appears to be the amide. This compound, which was formerly known as "pseudodiazoacetamide, $C_3HN_4(NH)_2(CONH_2)_3$," is now shown to be imidoazoacetamide, $NH{:}C(CONH_2)\cdot N{:}N\cdot C(CONH_2)NH$. Its constitution has been established chiefly by a comparative study of the action of reagents on this compound and on its isomerides in the other two series of polymeric derivatives of diazoacetamide, namely, the *C*- and *N*-*dihydrotetrazinedicarboxylamides*, the latter of which has been prepared for the first time. Of the reactions studied, that with alkalis may be taken as characteristic. In the case of the *C*- and *N*-dihydrotetrazinedicarboxylamides saponification occurs in a perfectly normal manner; neither substance shows any inclination to form salts as imidoazoacetamide does. In the presence of mercury, however, *N*-dihydrotetrazinedicarboxylamide forms a compound of such stability that prolonged boiling with concentrated sodium hydroxide entirely fails to saponify the amide. With pseudodiazoacetamide an imido-salt of the amide is first produced, as, for example, the ammonium salt $NH{:}C(CONH_2)N{:}N\cdot C(CONH_2)N(NH_4)$. It was the analysis of these salts which first showed the compound to be a dimolecular polymer of diazoacetamide. Secondary reactions subsequently occur thus (1) Baryta water on warming produces barium imidoazoacetate $\begin{matrix}N\cdot C(NH)CO_2\\ \|\\ N\cdot C(NH)CO_2\end{matrix}\!\!>\!Ba$. (2) The prolonged action of aqueous ammonia at ordinary temperatures gives rise to *iso*diazoacetamide, $CONH_2\cdot C\!<\!\begin{matrix}NH\\ \|\\ N\end{matrix}$ together with a small quantity of diazoacetamide. The constitution of the former was deduced chiefly from its action on benzaldehyde, with which it forms benzalazine, $N_2(CHC_6H_5)_2$. (3) Concentrated sodium hydroxide at 100° gives rise to bisdiazoacetic acid, $CO_2H\cdot CH\!<\!\begin{matrix}N{:}N\\ N{:}N\end{matrix}\!\!>\!CH\cdot CO_2H$.

The action of nitric oxide is also worthy of note as by its means either triazole nitrate, $CH\!<\!\begin{matrix}NH{:}HNO_3\\ N=\!=\!=N\end{matrix}\!\!>\!CH$ (a derivative of *N*-di-

hydrotetrazine), or bisazoxyacetic acid, $CO_2H{\cdot}CH<\begin{matrix}O\\N{-}N\\N{-}N\\O\end{matrix}>CH{\cdot}CO_2H$ (a derivative of *C*-dihydrotetrazine), can be obtained at will.

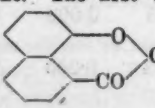
28. "Condensation of phenols with esters of unsaturated acids. Part VII." By S. Ruhemann.

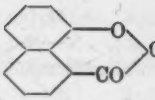
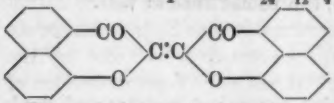
Benzo-1 : 4-pyrone (chromone) and its homologues have basic properties; they dissolve in hydrochloric acid to form hydrochlorides, and these solutions yield platinichlorides; but the salts are unstable and are decomposed by water with re-formation of the benzopyrones.

The author having been unable to obtain hydroxybenzo-1 : 4-pyrones from the dihydric phenols, has attempted to prepare them by starting from their mono-ethers, and from guaiacol and ethyl chlorofumarate has obtained ethyl guaiacoxyfumarate,

$$(\overset{(1)}{C}H_3O){\cdot}C_6H_4{\cdot}\overset{(2)}{O}{\cdot}C(CO_2Et){:}CH{\cdot}CO_2Et,$$

a yellow oil, b. p. 212—213° (at 15 mm.) and the corresponding acid (m. p. 138° with decomposition); on treatment of this acid with strong sulphuric acid a compound was obtained which is most probably methoxybenzo-1 : 4-pyronecarboxylic acid. This the author intends to transform into *O*-hydroxybenzo-1 : 4-pyrone.

It was further shown that the action of ethyl chlorofumarate on α-naphthol differs from the behaviour of the ester towards β-naphthol, for whilst with the latter it yields ethyl β-naphthoxyfumarate, $C_{10}H_7O{\cdot}C(CO_2Et){:}CH{\cdot}CO_2Et$, a yellow, fluorescent oil, b. p. 240—242° (pressure 12 mm.), which on hydrolysis is transformed into the corresponding acid, yellowish plates, m. p. 236° with decomposition, it reacts with α-naphthol to form in addition to a small quantity of ethyl α-naphthoxyfumarate, two substances which belong to a new class of compounds. One has the formula $C_{16}H_{12}O_4$, and crystallises in yellow needles, m. p. 146—147°; the other has the formula $C_{24}H_{12}O_4$, it forms orange needles which do not melt at 335°, are insoluble in the ordinary solvents, but dissolve in boiling nitrobenzene. The first compound is regarded as a derivative of the type  , called *naphtharone*, and as having the con-

stitution  , ethyl naphtharonylacetate, whilst the compound $C_{24}H_{12}O_4$ is represented by the formula  and termed *bisnaphtharonyl*.

Reasons for assigning these constitutions, and the description of some derivatives of these compounds, were given by the author.

29. "The chemical change produced by the immersion of lead in distilled water." By F. Clowes, D.Sc.

The author finds when very pure lead and ordinary distilled water were employed that much of the lead which underwent change passed into solution most probably as hydroxide, and was removable to a large extent from solution by passage through filter paper, from which it could again be entirely extracted by cold acetic acid. The compound of lead which remained undissolved by the water was found to have the formula $3PbCO_3,PbH_2O_2$.

In order to ascertain the respective parts played by atmospheric oxygen and carbon dioxide in solution, distilled water freed from dissolved gases by boiling was employed. When such water was placed in contact with lead in a vacuum or in an atmosphere of hydrogen, action only took place to the extent of 0·3 part of lead per million of water. When the water employed had been boiled in glass vessels and again exposed to air it never regained its full activity. This inhibitive effect varied with different glass vessels, being most marked in those kinds of glass which gave most dissolved matter to the water; contact of cold water and glass did not produce this effect, which was eliminated, however, in the experiments, the results of which are given below, by boiling the water employed in copper vessels.

The average results, expressed as percentages of lead in terms of the water employed, are shown in the following table:

	24 hours.	48 hours.	72 hours.
Oxygen alone	0·013	0·023	0·029
Carbon dioxide alone	0·005	0·008	0·017
Equal volumes of carbon dioxide and oxygen	0·003	0·003	0·003
Eight volumes of oxygen to one volume of carbon dioxide	0·015	0·018	—

This shows clearly that oxygen is the principal and primary agent, and that carbon dioxide exerts a restraining action in proportion to the volume present. It was found that carbon dioxide acted similarly in preventing solution of litharge.

The first action of aërated water apparently consists in oxidation and formation of hydroxide, which is precipitated as hydroxycarbonate by the carbon dioxide. The action is prevented or retarded by the presence of carbon dioxide in the initial stages. Total immersion of the lead also retards the action in presence of air, although the final result is the same whether the lead be wholly or only partially immersed in the water.

Of the substances which prevent this action, sulphuric acid and soluble sulphates are most effective, soluble carbonates are less so, whilst calcium hydroxide is still less so, but when present in larger quantity actually promotes the action.

30. "The bases contained in Scottish shale oil. Part I." By F. C. Garrett and J. A. Smythe.

The authors are continuing the examination of the bases contained in the Broxburn shale oil, of which a short account has been already given (*Proc.*, 1900, **16**, 190) and have completed the investigation of the portion boiling below 164°. The following bases have been isolated and identified:

Pyridine, b. p. 115—116° (in very small quantity).
α-Picoline, b. p. 129·5° (bar. 763 mm.).
αγ-Dimethyl pyridine, b. p. 159—159·5°.
αβ′- „ „ b. p. 154—155°.
αα′- „ „ b. p. 142·5° (bar. 760 mm.).
αγα′-Trimethyl pyridine, b. p. 170·5° (bar. 760 mm.).

αβ′-Dimethyl pyridine is a colourless liquid with a strong pyridine-like odour; it gives a picrate, m. p. 151—152°; a gold compound, m. p. 156—157°; a platinichloride containing 2 molecules of water and melting (when *anhydrous*) at 238° with decomposition; and a mercurichloride ($C_7H_9,HCl,6HgCl_2$) in very small, heavy crystals, m. p. 163°.

31. "Note on 'liquid nitrogen peroxide as a solvent.'" By P. F. Frankland, F.R.S., and R. C. Farmer, Ph.D.

In the authors' recent communication on "liquid nitrogen peroxide as a solvent" (*Trans.*, 1901, **79**, 1356), they inadvertently omitted to mention the previous work of Bruni and Berti (*Gazz. chim. Ital.*, 1900, **30**, ii, 151), of which they were not cognisant at the time.

It is fortunate that, whilst the two papers deal to some extent with the same subject, the experimental results do not to any great extent overlap, but rather supplement each other.

Bruni and Berti concerned themselves principally with cryoscopic measurements, and thus extended the still earlier work of Ramsay (*Trans.*, 1890, 57, 590), whereas the authors have investigated the electric conductivity and ebullioscopic behaviour of the solutions of a considerable number of different substances in the liquid peroxide, besides making a somewhat extensive examination of the action of the latter on a number of other substances, organic and inorganic.

The cryoscopic and ebullioscopic determinations agree in showing that the liquid peroxide is in many cases a powerfully associating solvent, and it is noteworthy that Bruni and Berti found acetic acid to be associated to triple molecules at the freezing point of the solvent, whilst the authors' measurements at the boiling point of the latter only revealed an association to double molecules.

The authors desire herewith to express their regret that the important work of these authors had escaped their attention.

ADDITIONS TO THE LIBRARY.

I. By Donation.

Ditte, Alfred. Introduction à l'étude des métaux. Pp. 488. Paris 1902. From the Author.

White, Edmund, and John Humphrey. Pharmacopedia, a commentary on the British Pharmacopœia, 1898. Pp. 696. Ill. London 1901. From the Authors.

II. Pamphlets.

Richards, Theodore William. The relation of the taste of acids to their degree of dissociation. II. (From *The Journal of Physical Chemistry*, vol. iv, No. 3, March, p. 207.) From the Author.

Richards, Theodore William. Suggestion concerning the nomenclature of heat capacity. (From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxvi, No. 18, January, 1901.) From the Author.

Richards, Theodore William. The possible significance of changing

atomic volume. (From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxvii, No. 1, June, 1901.) From the Author

Richards, Theodore William. The significance of changing atomic volume. II. The probable source of the heat of chemical combination, and a new atomic hypothesis. (From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxvii, No. 15, February, 1902.) From the Author.

Richards, Theodore William. Modification of Hempel's gas apparatus. (From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxvii, No. 10, November, 1901.) From the Author.

Richards, Theodore William, and Frank Roy Fraprie. The solubility of manganous sulphate. (From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxvi, No. 28, April, 1901.) From the Authors.

Richards, Theodore William, and Ebenezer Henry Archibald. The decomposition of mercurous chloride by dissolved chlorides: a contribution to the study of concentrated solutions. (From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxvii, No. 13, January, 1902.) From the Authors.

Richards, Theodore William, Charles F. McCaffrey, and Harold Bisbee. The occlusion of magnesic oxalate by calcic oxalate, and the solubility of calcic oxalate. (From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxvi, No. 22, April, 1901.) From the Authors.

Richards, Theodore William, and Benjamin Shores Merigold. A new investigation concerning the atomic weight of uranium. (From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxvii, No. 14, February, 1902.) From the Authors.

At the next meeting, on **Thursday, March 6th, at 8 p.m.**, the following papers will be communicated:

"The slow oxidation of methane at low temperatures." By W. A. Bone and R. V. Wheeler.

"Isomeric additive compounds of dibenzyl ketone and deoxybenzoin with benzal-*p*-toluidine, *m*-nitrobenzalaniline and benzal-*m*-nitraniline. Part III." By F. E. Francis.

"Mesoxalic semi-aldehyde." By H. J. H. Fenton and J. H. Ryffel.

"*m*-Nitrobenzoylcamphor." By M. O. Forster and Miss F. M. G. Micklethwait.

"Picrimidothiocarbonic esters." By J. C. Crocker.

"The identity of osyritin and myrticolorin." By A. G. Perkin.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 13/3/2

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. **No. 248.**

March 6th, 1902. Dr. DIVERS, F.R.S., Vice-President, in the Chair.

Messrs. W. G. Black, L. V. Turner, and H. Lucas were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs:

Ashe, James Samuel, The Adelaide Hospital, Dublin.
Cook, Arthur James, 167, Richmond Road, Hackney, N.E.
Dobson, Henry Arthur, Paisley Street, Orange, N.S.W.
Kewley, James, King's College, Cambridge.
Macknight, Alexander, Brucefield, Whitburn, N.B.
Martindale, William Harrison, 10, New Cavendish Street, W.
Peck, John Wicliffe, 28, West Ella Road, Harlesden, N.W.

The list of names of those recommended for election as Officers and Members of Council was read.

Of the following papers, those marked * were read:—

***32. "The slow oxidation of methane at low temperatures." By W. A. Bone and R. V. Wheeler.**

The authors have studied the slow oxidation of methane at temperatures between 300° and 400° in a supply of oxygen just sufficient to burn the carbon to carbon monoxide. The method adopted consisted in sealing mixtures of two volumes of methane and one volume of oxygen in bulbs of boro-silicate glass, which were maintained at constant temperatures of 300°, 325°, 350°, and 400° for periods of time

varying from 1 day to 3 weeks. The bulbs were afterwards examined and a careful analysis of the resulting mixture made.

The results indicate (1) that the disappearance of the oxygen is accompanied by a proportionate diminution in the volume of the cooled products, due to formation of water. (2) That at no stage of the process is either free hydrogen or free carbon liberated. (3) That a portion only of the methane is burnt, the carbon of which appears as carbon monoxide or dioxide, and the whole of the hydrogen as water. (4) That no other products can be detected at any stage of the oxidation.

Since the interaction of methane and oxygen at these temperatures is a 'surface' phenomenon, it is impossible to measure the relative velocities of the reaction at different temperatures, but evidence was obtained that the velocity increases with rising temperature. Thus at 300°, where the velocity is just appreciable, the disappearance of oxygen and formation of water can only be detected after the lapse of one or two weeks. At 400°, on the other hand, the whole of the oxygen always disappeared within a single day, and at 350°, in some instances, in three days.

Experiments have shown that similar bulbs containing electrolytic gas can be maintained at 350° for a week and at 400° for three days, without any visible formation of water occurring; at 400°, in one instance out of three, a marked formation of water took place in a week; in the other two bulbs, however, no change could be detected.

A study of the following possible secondary reactions at 325°, 350°, and 400°, namely (1) $CO + H_2O \rightleftharpoons CO_2 + H_2$, and (2) $2CO + O_2 = 2CO_2$, (moist) indicates that no complication arising from them enters into the methane-oxygen experiments. Further, it has been proved that the following substances do not react at 350—400°, namely (1) methane and steam, (2) methane and carbon dioxide, (3) carbon and steam.

The authors therefore conclude that the first stage of the oxidation of methane at these temperatures does not consist of a '*selective combustion*' of either hydrogen or carbon, but in a *simultaneous oxidation of carbon and hydrogen*, as represented by the equation $2CH_4 + 3O_2 = 2CO + 4H_2O$.

The occurrence of carbon dioxide in the products (and in many cases as much as one-third to one-half of the carbon burnt appears as the dioxide) cannot be explained on the supposition that carbon monoxide liberated in the primary oxidation is subsequently *gradually* oxidised through the agency of steam and oxygen, or steam alone. The more probable explanation is that the carbon monoxide and steam molecules which simultaneously come into being in the primary oxidation are, *at the moment of formation*, in a very labile and reactive condition, and this would favour the rapid exchange of oxygen in the system,

$\begin{matrix} CO \\ CO \end{matrix} \Big| \begin{matrix} OH_2 \\ OH_2 \end{matrix} \Big| O_2$. The carbon dioxide is mainly, if not entirely, produced during this short 'labile period.'

***33. "Isomeric additive compounds of dibenzylketone and deoxybenzoin with benzal-*p*-toluidine, *m*-nitrobenzalaniline, and benzal-*m*-nitraniline. Part III." By F. E. Francis, B.Sc., Ph.D.**

The additive compounds formed with dibenzylketone and deoxybenzoin with benzal-*p*-toluidine were unstable and consequently unsatisfactory for confirming the existence of the so-called α-, β-, and γ-modifications. In the case of dibenzylketone and *m*-nitrobenzalaniline the β-modification obtained by recrystallisation of the α-form from benzene containing traces of piperidine melted 31° higher, and with dibenzylketone and benzal-*m*-nitraniline 43° higher than the α-additive product; in the latter case, there was also a distinct change in the solubility and appearance of the β-form. These were considered satisfactory confirmations of the individuality of the β-modification, because in cases previously investigated the rise in melting point was never greater than 10—12°, and since the β-modifications were transformed into the α- by means of heat, this small difference in melting point was not very satisfactory. α-Dibenzylketone benzal-*m*-nitraniline on recrystallisation from benzene containing traces of sodium ethoxide appears to be converted into the γ-modification, and the melting point rises from 134° to 182·3°, but this was the only case observed. Substances of much higher melting point and smaller solubility, and apparently belonging to neither α-, β-, or γ-modifications, were obtained in the case of deoxybenzoin and benzal-*p*-toluidine, deoxybenzoin and benzal-*m*-nitraniline, and dibenzylketone and *m*-nitrobenzalaniline. These are similar in molecular weight and composition to the isomerides of lower melting point, and it is interesting to note that whereas dibenzylketone and benzal-*m*-nitraniline give a pure α-additive compound, deoxybenzoin with the same substance only gives the isomeride of higher melting point.

Discussion.

Dr. Lowry asked if it was not possible that one of the three modifications described by the author as the α-, β- and γ-forms might be a stable mixture of two isomerides and not a single chemical compound. In the case of the three modifications of π-bromonitrocamphor, those melting at 108° and 142° were found to be the normal and pseudo-nitro-compounds respectively, whilst that melting at 126° was only a stable mixture of these two.

Dr. FRANCIS, in reply, said that he had been unable to obtain any evidence that any of the modifications described was a mixture, and that if they were mixed they could be again separated by fractional crystallisation.

***34. "Mesoxalic semi-aldehyde." By H. J. H. Fenton, F.R.S., and J. H. Ryffel, B.A., B.Sc.**

Chlorine is slowly absorbed by a solution of tartaric acid containing iron in the ferrous state, and the product, after removal of the unaltered tartaric acid, is found to have powerful reducing and other aldehyde properties. With phenylhydrazine, it yields a bright orange precipitate having the composition $C_{15}H_{14}N_4O_2$, which is identical in every respect with the osazone obtained by Nastvogel from dibromopyruvic acid (*Annalen*, 1888, 248, 85) and by Will from collodion-wool (*Ber.*, 1891, 24, 400 and 3831).

A re-investigation, however, proves that the true melting point of this osazone is 222—224° instead of the lower number, 201—207°, ascribed to it by various authors. This osazone has the constitution $CH{:}N_2HPh{\cdot}C{:}N_2HPh{\cdot}CO_2H$ and corresponds either to hydroxypyruvic acid, tartronic semi-aldehyde, or mesoxalic semi-aldehyde.

With hydroxylamine, however, the *dioxime*, $CHNOH{\cdot}CNOH{\cdot}CO_2H$, or dioximidopropionic acid is obtained identical with that prepared by Söderbaum from dibromopyruvic acid (*Ber.*, 1892, 25, 904) and by oxidation with cupric hydroxide in alkaline solution *mesoxalic acid* results.

Since the oxidation product is free from chlorine, these facts leave no room for doubt as to the nature of the substance in question, namely, that it is the semi-aldehyde of mesoxalic acid.

Its formation from tartaric acid in the manner above described is due to the initial production of dihydroxymaleic acid, and it may be prepared in a pure state directly from the latter acid by the action of ferric salts. With ferric sulphate or chloride, for example, the change takes place almost quantitatively according to the equation: $C_4H_4O_6 + Fe_2(SO_4)_3 = C_3H_2O_4 + 2FeSO_4 + H_2SO_4 + CO_2$.

After removal of the iron salt and free mineral acid, the product is obtained as a thick syrup, which, so far, has not been induced to crystallise. The derivatives and transformations of this aldehyde-acid are being further investigated.

***35. "The action of hydrogen peroxide on carbohydrates in the presence of ferrous salts. III." By R. S. Morrell and J. M. Crofts.**

The specific action of hydrogen peroxide in the presence of ferrous sulphate was first demonstrated by Fenton in the oxidation of tartaric acid to dihydroxymaleic acid (*Trans.*, 1894, 65, 899). Glucose, lævulose, arabinose, and rhamnose have been shown by the authors to be transformed by this peculiar reaction into osones, which were recognised by their power to react with substituted hydrazines at the ordinary temperature (*Trans.*, 1899, 75, 786, and 1900, 77, 1219) It has been found that mannose on oxidation gave an osone which yielded with phenylhydrazine at the ordinary temperature phenylglucosazone. The preparation of pure glucosone from both glucose and lævulose has been attempted, and a white, amorphous solid has been obtained which gave analytical results agreeing with the formulæ $C_6H_{12}O_6$ and $C_6H_{10}O_6$. This substance reacted readily with phenylhydrazine at the ordinary temperature and furnished a good yield of phenylglucosazone. The glucosone from glucose was feebly dextrorotatory, whilst that from lævulose was slightly lævorotatory. Glucosone obtained by E. Fischer (*Ber.*, 1889, 22, 87) is lævorotatory.

An aqueous solution of glucosone prepared from either glucose or lævulose on oxidation with bromine at 40° furnished a good yield of the calcium salt of a trioxybutyric acid. The barium salt of the same acid has been obtained, and both the calcium and barium salts seem to be identical with *d*-erythronic acid (Ruff, *Ber.*, 1899, 32, 3678). The calcium and barium salts of this acid obtained from glucosone prepared from either dextrose or lævulose have yielded butyric acid on reduction with hydriodic acid and phosphorus.

***36. "*m*-Nitrobenzoylcamphor." By M. O. Forster and Miss F. M. G. Micklethwait.**

α′-m-*Nitrobenzoyl*-α-*bromocamphor*, $C_8H_{14}<\begin{matrix}CBr\cdot CO\cdot C_6H_4NO_2\\ CO\end{matrix}$, prepared from α′-benzoyl-α-bromocamphor and fuming nitric acid, separates from methyl alcohol in pale yellow, flat, prismatic needles melting at 93—94°; a 2 per cent. solution in chloroform has $[\alpha]_D = +87{\cdot}9°$. α-m-*Nitrobenzoyl*-α′-*bromocamphor*, obtained in a similar manner from the isomeric benzoylbromocamphor, crystallises in aggregates of small, pale yellow needles and melts at 101—102°; a 2 per cent. solution in chloroform has $[\alpha]_D = -26{\cdot}1°$.

Enolic m-*nitrobenzoylcamphor*, $C_8H_{14}<\begin{matrix}C\cdot CO\cdot C_6H_4NO_2\\ \|\\ C\cdot OH\end{matrix}$, formed on

reducing the nitrobenzoylbromocamphors with alcoholic potash, crystallises from alcohol in long, pink, silky needles melting at 106—107°; it has not been obtained in the ketonic form, but the specific rotation of a 2 per cent. solution in chloroform, having $[\alpha]_D = +209{\cdot}5°$ when freshly prepared, falls to $+200{\cdot}1°$ in the course of several days, indicating slight transformation into the isomeride. *m*-Nitrobenzoylcamphor dissolves in aqueous alkali hydroxides and the alcoholic solution develops an intense purple coloration with ferric chloride; oxidation with potassium permanganate gives rise to camphoric and *m*-nitrobenzoic acids. The *acetyl* derivative crystallises from light petroleum in pale brown needles and melts at 127—128°.

Enolic o-nitrobenzoylcamphor crystallises from alcohol in pale brown, transparent prisms and melts at 118°; a 2 per cent. solution in chloroform has $[\alpha]_D = +44{\cdot}5°$ when freshly prepared, and $+60{\cdot}5°$ after an interval of several days.

α'-m-Nitrobenzoyl-α-chlorocamphor, $C_8H_{14}\begin{cases}CCl\cdot C_6H_4NO_2\\ CO\end{cases}$, crystallises from alcohol in aggregates of pale yellow prisms and melts at 72—74°; a 2 per cent. solution in chloroform has $[\alpha]_D = +40{\cdot}4°$.

α-m-Nitrobenzoyl-α'-chlorocamphor separates from alcohol in small, nearly colourless needles and melts at 110°; a 2 per cent. solution in chloroform has $[\alpha]_D = +7{\cdot}1°$. When these isomerides are heated with alcoholic potash, enolic *m*-nitrobenzoylcamphor is not formed; the sole products are α-chlorocamphor and *m*-nitrobenzoic acid.

*37. "The Cloëz reaction." By F. D. Chattaway and J. M. Wadmore.

The reaction between cyanogen chloride or bromide and an alcoholic solution of sodium ethylate appears at first sight to be inconsistent with the nitrogen halogen constitution which we have shown cyanogen chloride and bromide to possess. It becomes intelligible, however, when we consider the behaviour of the nitrogen halogen linkage towards alcohol.

Halogen attached to nitrogen reacts very readily with alcohol, the halogen being invariably replaced by hydrogen and a hypohalogen ester formed thus: $:N-X+C_2H_5OH=:N\cdot H+C_2H_5OX$.

The interaction of ethyl alcohol and trichloriminocyanuric acid, when ethyl hypochlorite and cyanuric acid are produced, is a simple case. In the Cloëz reaction, cyanogen chloride or bromide first reacts with the alcohol as a typical nitrogen halogen compound, forming hydrocyanic acid and ethyl hypochlorite or hypobromite, thus: $C:N\cdot Cl+C_2H_5OH=C:N\cdot H+C_2H_5OCl$.

These then combine and form ethyl iminochlorocarbonate, the hydrocyanic acid, or sodium cyanide, since sodium ethylate is present, behaving as an unsaturated substance: $C_2H_5OCl + C{:}N{\cdot}H = \begin{matrix} C_2H_5O \\ Cl \end{matrix} > C{:}N{\cdot}H$.

The ethyl iminochlorocarbonate then reacts in various ways to form the different substances which have been isolated from the product of the action, for example, it reacts with alcohol to form diethyl iminocarbonate, with water to form urethane, whilst three molecules interact with elimination of hydrogen chloride to produce normal triethyl cyanurate.

Discussion.

Professor Tilden thought Dr. Chattaway had brought forward a body of evidence which practically established his case, but he would like to inquire whether the production of a nitrile, by interaction between a common cyanide and a haloid compound, had engaged the attention of the authors, and what explanation they would give of the mechanism of the change. In such interactions, carbon appears to be directly attached to carbon, and there is no evidence of even a temporary formation of a compound in which the cyanide group is linked on by means of the nitrogen.

Dr. Chattaway, in reply, stated that the imino-structure of cyanides admitted of action occurring in three ways, addition to the nitrogen, or to both nitrogen and carbon, or to carbon, taking place thus: $H{\cdot}N{:}C + X_2 = HX_2{:}N{:}C$; or $H{\cdot}N{:}C + X_2 = H{\cdot}NX{\cdot}CX$; or $H{\cdot}N{:}C + X_2 = H{\cdot}N{:}C{:}X_2$, the mode of interaction in any particular case and the further secondary changes being determined by the nature of the cyanogen derivative and by that of the substance interacting with it. All reactions of these compounds could be formulated according to one or other of these types. The imino-formulæ of the cyanides are capable of expressing conventionally three phases of atomic relationship, the atoms composing a single molecule can only be in one phase at any instant, but the particular phase at which it reacts is determined by a related phase of the interacting molecule.

38. "The picrimidothiocarbonic esters." By J. C. Crocker, B.A.

When picryl chloride is treated with ammonium thiocyanate in alcoholic solution, a reaction readily takes place from which a well crystallised yellow substance is obtained, having the empirical formula $C_{15}H_9N_7SO_{13}$. On hydrolysis, it yields picramide. The reaction may be thus explained. Picryl thiocarbimide, $Pi{\cdot}N{:}C{:}S$, is probably the first product. A molecule of this substance adds on another molecule of picryl chloride, the chlorine atom becoming attached to the carbon

atom and the picryl group to the sulphur atom. The acid chloride thus formed reacts with the alcohol to form a picrimidopicrylthiocarbonic ester with the elimination of hydrochloric acid. Thus:

$$Pi{\cdot}N{:}C{:}S + PiCl \longrightarrow Pi{\cdot}N{:}C\begin{matrix}Cl\\S-Pi\end{matrix} \longrightarrow Pi{\cdot}N{:}C\begin{matrix}Cl\\S{\cdot}Pi\end{matrix} +$$

$$EtOH \longrightarrow PiN{:}C\begin{matrix}OEt\\S{\cdot}Pi\end{matrix}$$

Similar substances have also been prepared from methyl, propyl, and *iso*butyl alcohols. In the case of methyl alcohol, two substances have been obtained, which are stereoisomeric, corresponding to the "syn-" and "anti-" forms of the oximes

$$CH_3{\cdot}O{\cdot}\overset{\displaystyle N{\cdot}Pi}{\overset{\|}{C}}{\cdot}S{\cdot}Pi \quad \text{and} \quad CH_3{\cdot}O{\cdot}\overset{\displaystyle Pi{\cdot}N}{\overset{\|}{C}}{\cdot}S{\cdot}Pi .$$

39. "Robinin, violaquercetin, myrticolorin and osyritrin." By A. G. Perkin.

In continuation of the research of which a preliminary account has already been given (*Proc.*, 1901, **17**, 87), the author has re-examined the properties of myrticolorin, $C_{27}H_{28}O_{16}$, a quercetin glucoside present in *Eucalyptus macrorhyncha*, which, as described by H. G. Smith (*Trans.*, 1898, **73**, 697), differed mainly from osyritrin (*Proc.*, 1901, **17**, 87) in that the sugar derived from it appeared to be galactose. As Smith (private communication) finds on re-examination that this is dextrose, comparative experiments have been carried out. The results show that myrticolorin is identical with osyritrin.

40. "The nitration of *s*-trihalogen anilines." By K. J. P. Orton.

The carefully regulated action of nitric acid on the six *s*-trihalogen anilines, *s*-tribromoaniline, 2-chloro-4 : 6-dibromoaniline, 2 : 6-dichloro-4-bromoaniline, 4-chloro-2 : 6-dibromoaniline, 2 : 4-dichloro-6-bromoaniline, and *s*-trichloroaniline has been investigated. The anilines were dissolved (or suspended) in glacial acetic acid; to the solution nitric acid free from nitrous acid was added; the mixture, which now contained crystalline aniline nitrate, was heated on the water-bath. From their behaviour when this mixture is heated, the anilines may be sharply divided into two classes, namely, those with a bromine atom in the para-position relative to the amino-group and those with a chlorine atom in the para-position. With the first, the nitrate of the aniline dissolves quickly, forming an orange solution, which becomes gradually more yellow in colour and gives off bromine; on cooling, an aniline crystallises out, in which the *p*-bromine atom has been replaced by a nitro-group; thus, from *s*-tribromoaniline, 2 : 6-dibromo-4-nitroaniline

is obtained (compare Losanitsch, *Ber.*, 1882, 15, 474); from 2-chloro-4 : 6-dibromoaniline, 2-chloro-6-bromo-4-nitroaniline (m. p. 177°), and from 2 : 6-dichloro-4-bromoaniline, 2 : 6-dichloro-4-nitroaniline are obtained. Secondly, when a chlorine atom is in the para-position, a solution is obtained, transiently of a purple colour, which quickly passes to magenta and then slowly to a deep crimson. No chlorine or bromine is evolved, nor are anilines detectable in which a bromine atom in an ortho-position or the chlorine atom in the para-position has been replaced by the nitro-group.

During the period of heating there can be isolated from the solutions of both the above classes of anilines a small quantity of the corresponding nitroamines; thus, from *s*-tribromoaniline is obtained *nitroamino*-2 : 4 : 6-*tribromobenzene*, slender flesh-coloured needles (from water) melting and decomposing at 143—144°; and from *s*-trichloroaniline, *nitroamino*-2 : 4 : 6-*trichlorobenzene*, slender flesh-coloured needles (from water) melting and decomposing at 135°. In solution in acetic acid, in the presence of a trace of a mineral acid, the nitroamines themselves undergo change, that from *s*-tribromoaniline yielding 2 : 6-dibromo-4-nitroaniline, whereas that from *s*-trichloroaniline yields a characteristic crimson solution. From the crimson solution can be isolated a small quantity of a *red* crystalline substance, melting and decomposing at 143°. Experiments on the preparation of this and allied substances are now in progress.

41. "Some *s*-nitrochlorobromoanilines and their derivatives." By K. J. P. Orton.

The following anilines, acetanilides, diacetanilides, and chloroamino-derivatives have been prepared in connection with the investigation described in the preceding communication.

2-*Chloro*-6-*bromo*-4-*nitroaniline*, $C_6H_2ClBr(NO_2)\cdot NH_2$, prepared by chlorinating 2-bromo-4-nitroaniline, long, yellow, prismatic needles melting at 177°; 2-*chloro*-6-*bromo*-4-*nitroacetanilide*, $C_6H_2ClBr(NO_2)\cdot NHAc$, slender, colourless prisms melting at 221—222°; 2-*chloro*-6-*bromo*-4-*nitrodiacetanilide*, $C_6H_2ClBr(NO_2)\cdot NAc_2$, colourless four-sided prisms melting at 134°; *acetylchloroamino*-2-*chloro*-6-*bromo*-4-*nitrobenzene*, $C_6H_2ClBr(NO_2)\cdot NClAc$, white, lustrous prisms melting at 84—85°. 2-*Chloro*-4-*bromo*-6-*nitroaniline*, $C_6H_2ClBr(NO_2)\cdot NH_2$, silky, yellow needles melting at 114°; 2-*chloro*-4-*bromo*-6-*nitroacetanilide*, $C_6H_2ClBr(NO_2)\cdot NHAc$, prepared by nitrating 2-chloro-4-bromoacetanilide, white needles or prisms melting at 194°; *acetylchloroamino*-2-*chloro*-4-*bromo*-6-*nitrobenzene*, $C_6H_2ClBr(NO_2)\cdot NClAc$, long, pale yellow, lustrous, very soluble prisms melting at 56—57°. 4-*Chloro*-2-*bromo*-

6-nitroaniline, $C_6H_2ClBr(NO_2)\cdot NH_2$, silky, yellow needles melting at 114—115°; *4-chloro-2-bromo-6-nitroacetanilide*, $C_6H_2ClBr(NO_2)\cdot NHAc$, prepared by nitrating 4-chloro-2-bromoacetanilide, white prisms melting at 207°. *Acetylchloroamino-2 : 6-dibromo-4-nitrobenzene*, $C_6H_2Br_2(NO_2)\cdot NClAc$, small, lustrous, four-sided prisms, with domed ends, melting at 110—111°. 2 : 4-*Dibromo-6-nitrodiacetanilide*, $C_6H_2Br_2(NO_2)\cdot NAc_2$, prepared by boiling the aniline with excess of acetic anhydride, aggregates of prisms or rhombs melting at 96—97°. 2 : 3 : 4 : 6-*Tetrabromoacetanilide*, $C_6HBr_4\cdot NHAc$, prepared from tetrabromoaniline, silky, white needles melting at 228—229°; 2 : 3 : 4 : 6-*tetrabromodiacetanilide*, $C_6HBr_4\cdot NAc_2$, lustrous, four-sided prisms with domed ends, melting at 164°. 2 : 3 : 6-*Tribromo-4-nitroaniline*, $C_6HBr_3(NO_2)\cdot NH_2$, prepared by brominating 3-bromo-4-nitroaniline, pale lemon-yellow needles melting at 155—155·5°. 2 : 3 : 4-*Tribromo-6-nitroaniline*, $C_6HBr_3(NO_2)\cdot NH_2$, prepared from 3-bromo-6-nitroaniline, orange-yellow needles melting at 165·5—166°; 2 : 3 : 4-*tribromo-6-nitroacetanilide*, $C_6HBr_3(NO_2)\cdot NHAc$, colourless, flattened needles melting at 221°.

42. "The resolution of pheno-α-aminoheptamethylene into its optical isomerides. Tartrates of pheno-α-aminoheptamethylene and of hydrindamine." By F. S. Kipping and A. E. Hunter.

An investigation of the salts produced by the combination of *dl*-pheno-α-aminoheptamethylene with tartaric acid has shown that this base behaves quite differently from *dl*-hydrindamine (pheno-α-aminopentamethylene) in spite of the similarity in constitution of the two bases.

dl-*Pheno-α-aminoheptamethylene*-d-*tartrate*, $2C_{11}H_{15}N,C_4H_6O_6+\frac{1}{2}H_2O$, separates from neutral and from acid solutions of the *dl*-base in aqueous tartaric acid, in lustrous prisms decomposing at about 235°; in aqueous solution $[\alpha]_D = +13°$.

l-*Pheno-α-aminoheptamethylene hydrogen* d-*tartrate*, $C_{11}H_{15}N,C_4H_6O_6+3H_2O$, is obtained when the solution of the normal tartrate is mixed with excess of tartaric acid and fractionally crystallised; it forms slender prisms and melts at 181—182°; its aqueous solutions are feebly lævorotatory ($[\alpha]_D = -1·6°$ approximately).

l-*Pheno-α-aminoheptamethylene* d-*tartrate*, $2C_{11}H_{15}N,C_4H_6O_6$, prepared from the *l*-base, crystallises in transparent, triangular plates and decomposes at 215—217°. The *hydrochloride* of the *l*-base forms lustrous prisms, and in dilute aqueous solution its specific rotation is $[\alpha]_D = +24°$.

Benzoyl-l-*pheno-α-aminoheptamethylene*, $C_{11}H_{14}N\cdot COPh$, crystallises in needles, melts at 175—176°, and is dextrorotatory in methyl alcoholic solution.

d-*Pheno-α-aminoheptamethylene* d-*tartrate*, $2C_{11}H_{15}N,C_4H_6O_6$, can be isolated from the mother liquors obtained after separating the hydrogen salt of the *l*-base; it is anhydrous and decomposes at about 216—217°.

d-*Pheno-α-aminoheptamethylene hydrogen tartrate*, $C_{11}H_{15}N,C_4H_6O_6$, prepared by treating the normal salt with tartaric acid, decomposes at about 205—206°.

dl-*Hydrindamine hydrogen* d-*tartrate*, $C_9H_{11}N,C_4H_6O_6+H_2O$, crystallises in slender needles, melts at 168—169°, and is not resolved or changed in any way by repeated crystallisation from water. The normal d-*tartrate* of the *dl*-base forms plates melting at about 200° and dissociates hydrolytically in aqueous solution.

l-*Pheno-α-aminoheptamethylene* d-*bromocamphorsulphonate*,

$$C_{11}H_{15}N,C_{10}H_{14}BrO\cdot SO_3H,$$

crystallises in prisms melting at 216—217°; in dilute aqueous solution $[\alpha]_D = +47{\cdot}8°$.

ADDITIONS TO THE LIBRARY.

I. By Donation.

Landauer, John. Blowpipe analysis. Pp. 173. London 1901. From the Publishers.

Remsen, Ira. A college text-book of chemistry. Pp. 689. London 1901. From the Publishers.

Söderbaum, Henrik Gustav. Jac. Berzelius. Sjalfbiografiska anteckeningar. Utgifna af Kongl. Svenska Vetenskapsakademien genom H. G. S. Pp. 246. Stockholm 1901. From C. P. Sandberg.

Travers, Morris William. The experimental study of gases. An account of the experimental methods involved in the determination of the properties of gases, and of the more important researches connected with the subject. Pp. 323. London 1901. From the Publishers.

II. Purchase.

Elbs, Karl. Übungsbeispiele für die elektrolytische Darstellung chemischer Präparate. Zum Gebrauch in Laboratorium für Chemiker und Elektrochemiker. Pp. 100. Ill. Halle-a-S. 1902.

Encomium Argenti Vivi. A treatise upon the use and properties of quicksilver, or, the natural, chemical, and physical history of that surprising mineral, extracted from the writings of the best naturalists, chemists, and physicians. Wherein its various operations are accounted

for, and the use of it recommended: with some remarks upon the animadversions of Dr. Turner upon belloste. London.

ANNUAL GENERAL MEETING.

The Annual General Meeting of the Society, for the election of Officers and Council, and for other business, will be held on **Wednesday**, March 26th, at **half-past four** o'clock in the afternoon.

RAOULT MEMORIAL LECTURE.

The Raoult Memorial Lecture will be delivered by Professor van't Hoff, on **Wednesday**, March 26th, at **9** p.m.

This Lecture will be delivered, by **kind permission of the Managers**, in the Theatre of the Royal Institution, Albemarle Street, W.

Admission will be by ticket only. Each Fellow of the Society will be entitled to two tickets, which may be obtained on application to the Assistant Secretary, Chemical Society, Burlington House.

At the next meeting, on **Wednesday, March 19th, at 5.30** p.m., the following papers will be communicated:

"The absorption spectra of metallic nitrates. Part I." By W. N. Hartley.

"A method of determining the ratio of distribution of a base between two acids." By H. M. Dawson and F. E. Grant.

"On the molecular complexity of acetic acid in chloroform solution." By H. M. Dawson.

"On the existence of polyiodides in nitrobenzene solution." By H. M. Dawson and R. Gawler.

"Nitrogen chlorides containing the propionyl groups." By F. D. Chattaway.

"Derivatives of α-aminocamphoroxime." By A. Lapworth and A. W. Harvey.

"Preparation of sulphamide from ammonium amidosulphite." By E. Divers and M. Ogawa.

"Hypoiodous acid." By R. L. Taylor.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY

Issued 26/3/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. **No. 249.**

Wednesday, March 19th, 1902. Professor EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

Messrs. Catchpole, Green, and Hanson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs:

Clowes, George H. A., Gratwick Research Laboratory, Buffalo, U.S.A.
Crookes, Henry, 109, Ladbroke Grove, W.
Everitt, Walter, 83, The Grove, Ealing, W.
Gill, J. Arthur, 19, Burma Road, Stoke Newington, N.
Griffiths, John T., Grammar School, Hanley Castle, Worcestershire.
King, Sidney Isaac, 49, Arundel Square, N.
Mathieson, Robert, Rillbank, Innerleithen, Peebleshire.
Mence, George Augustus Henry, Ouse Villa, St. Ives, Hunts.
Taylor, Thomas, 12, Ancaster Drive, Great Western Road, W.
Wood, Frank Stanley, 25, Suffolk Street, Newland, Hull.

The SECRETARY announced that the Treasurer, Professor TILDEN, had represented the Society at the recent celebration of the Jubilee of The Owens College, Manchester, and had presented the following congratulatory Address from the Society:

"The President, Council, and Fellows of the Chemical Society desire on this the present occasion of the celebration of the Fiftieth Anniversary of the foundation of Owens College to express their high appreciation of the conspicuous services rendered to the cause of scientific education by the foundation and ever increasing activity of the College.

"They recall with especial satisfaction the contributions to Chemical Science which have emanated from the laboratories of Owens College under the direction of the successive eminent Professors of Chemistry, who must be regarded as the immediate scientific successors of John Dalton, the founder of Modern Chemistry. With sincere wishes for the future development and extended usefulness of the College they desire to tender to the President, Council, Fellows and Students an expression of hearty congratulation on the celebration of this their Jubilee.

J. EMERSON REYNOLDS, *President.*
WILLIAM A. TILDEN, *Treasurer.*
WYNDHAM R. DUNSTAN,
ALEXANDER SCOTT,
RAPHAEL MELDOLA, } *Secretaries.*"

Of the following papers those marked * were read:—

*43. "Nitrogen chlorides containing the propionyl group." By F. D. Chattaway.

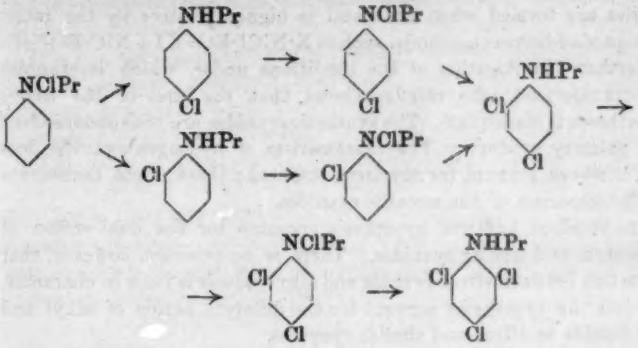
Aniline and the chloro-substituted anilines readily yield propionyl derivatives, which, on treatment with excess of hypochlorous acid, are converted into substituted nitrogen chlorides. In these reactions, hypochlorites are probably first formed, the nitrogen developing its higher valency, water being subsequently eliminated. The reaction is a reversible one:

$$\begin{matrix} R \\ Pr \end{matrix}\!\!>\!NH + HOCl \rightleftarrows \begin{matrix} R \\ Pr \end{matrix}\!\!>\!N\!\!<\!\!\begin{matrix} H \\ OH \\ Cl \end{matrix} \rightleftarrows \begin{matrix} R \\ Pr \end{matrix}\!\!>\!N{\cdot}Cl + H_2O\,.$$

These nitrogen chlorides show all the characteristic reactions of the group, the chief feature of such reactions being the invariable replacement of the halogen by hydrogen.

When there is hydrogen, either in the para- or the ortho-position,

transformation of the nitrogen chloride into the isomeric substituted anilide readily takes place according to the scheme:



The following compounds have been prepared:—*Chloroiminopropionanilide*, $C_6H_5\cdot NCl\cdot COC_2H_5$, colourless plates, m. p. 77°; p-*chloropropionanilide*, $C_6H_4Cl\cdot NH\cdot COC_2H_5$, plates, m. p. 141°; *chlorimino*-p-*chloropropionanilide*, $C_6H_4Cl\cdot NCl\cdot COC_2H_5$, colourless plates, m. p. 55°, *bromoimino*-p-*chloropropionanilide*, $C_6H_4Cl\cdot NBr\cdot COC_2H_5$, yellow prisms, m. p. 71°; o-*chloropropionanilide*, $C_6H_4Cl\cdot NH\cdot COC_2H_5$, colourless plates, m. p. 91°; *chloroimino*-o-*chloropropionanilide*, $C_6H_4Cl\cdot NCl\cdot COC_2H_5$, colourless plates, m. p. 57°; *bromoimino*-o-*chloropropionanilide*, $C_6H_4Cl\cdot NBr\cdot COC_2H_5$, pale yellow prisms, m. p. 106°; 2 : 4-*dichloropropionanilide*, $C_6H_3Cl_2\cdot NH\cdot COC_2H_5$, colourless prisms, m. p. 121°; *chloroimino*-2 : 4-*dichloropropionanilide*, $C_6H_3Cl_2\cdot NCl\cdot COC_2H_5$, colourless plates, m. p. 64°; *bromoimino*-2 : 4-*dichloropropionanilide*, $C_6H_3Cl_2\cdot NBr\cdot COC_2H_5$, pale yellow rhombs, m. p. 66°; 2 : 4-*trichloropropionanilide*, $C_6H_2Cl_3\cdot NH\cdot COC_2H_5$, colourless prisms, m. p. 161°; *chloroimino*-2 : 4 : 6-*trichloropropionanilide*, $C_6H_2Cl_3\cdot NCl\cdot COC_2H_5$, pearly plates, m. p. 80°; *bromoimino*-2 : 4 : 6-*trichloropropionanilide*, $C_6H_2Cl_3\cdot NBr\cdot COC_2H_5$, bright yellow plates, m. p. 106°.

***44. "The constitution of the metallic cyanides as deduced from their synthetic interactions: the constitution of hydrogen cyanide." By J. Wade.**

The formation of both nitriles and isocyanides from metallic cyanides has been explained in three ways: (1) the metallic cyanides are isocyanides, and yield isocyanides by direct interchange; nitriles are formed subsequently by isomeric change; (2) hydrogen cyanide is

tautomeric and forms two classes of metallic salts (Laar); (3) the metallic cyanides are isocyanides and yield isocyanides as in (1); nitriles are formed when the metal is highly positive by the intervention of additive compounds, such as $K\cdot N{:}Cl\cdot Et = KI + N{\vdots}C\cdot Et$ (Nef).

Further investigation of the conditions under which isocyanides are transformed into nitriles shows that the first of the above hypotheses is inadequate. The synthetic cyanides are thus independent and primary products. The tautomerism of hydrogen cyanide does not, however, account for the facts observed; these would necessitate the tautomerism of the metallic cyanides.

The third or additive hypothesis accounts for the dual action of potassium and similar cyanides. There is no evidence, however, that the action between silver cyanide and alkyl haloids is ionic in character, nor does the hypothesis account for the different action of alkyl and acyl haloids on silver and similar cyanides.

The action of alkyl iodides on silver cyanide is parallel to their action on alkyl isocyanides, the alkyl in each case combining with the nitrogen of the cyanogen group, whereas in the action of acyl halogen compounds the acyl combines with the carbon. The alkyl radicles are feebly electropositive, the acyl electronegative; the additive power of the unsaturated carbon of the isocyanides is thus dependent not merely on the electrochemical character of the attached radicle, as Nef postulates, but on its electrochemical position relatively to the radicle of the interacting halogen compound.

When the metal or alkyl of the isocyanide is sufficiently positive with regard to the radicle of the interacting molecule, the latter combines with the carbon of the isocyanogen group, but when the two radicles are electrochemically adjacent, the interacting molecule combines with the nitrogen:

$$\left\{\begin{array}{l} K\cdot N{:}C + EtI = K\cdot N{:}Cl\cdot Et = KI + N{\vdots}C\cdot Et \\ K\cdot N{:}C + EtKSO_4 = K\cdot N{:}C(SO_4K)\cdot Et = K_2SO_4 + N{\vdots}C\cdot Et \\ \quad + \qquad\quad + \\ \text{strongly} \quad \text{feebly} \end{array}\right.$$

$$\left\{\begin{array}{l} Et\cdot N{:}C + EtI = Et.NEtI{:}C \quad (\rightarrow NHEt_2) \\ Ag\cdot N{:}C + EtI = Ag\cdot NEtI{:}C = AgI + NEt{:}C \\ \quad + \qquad\quad + \\ \text{feebly} \quad \text{feebly} \end{array}\right.$$

$$\left\{\begin{array}{l} Et\cdot N{:}C + AcCl = Et\cdot N{:}CCl\cdot Ac \quad (\rightarrow CH_3\cdot CO\cdot CO_2H) \\ Ag\cdot N{:}C + AcCl = Ag\cdot N{:}CCl\cdot Ac = AgCl + N{\vdots}C\cdot Ac \quad (\rightarrow CH_3\cdot CO\cdot CO_2H) \\ Cu\cdot N{:}C + PhN{:}N\cdot Cl = Cu\cdot N{:}CCl\cdot N{:}NPh = CuCl + N{\vdots}C\cdot N{:}NPh \\ \quad + \qquad\quad - \\ \text{feebly} \quad \text{strongly} \end{array}\right.$$

The principle of this hypothesis is applicable to other similar cases of dual action.

The reactions which indicate an isocyanic constitution for hydrogen cyanide are also susceptible of an opposite interpretation. The physical and physiological properties of hydrogen cyanide also correspond with those of the nitriles.

It is probable that the metallic cyanides are, as Gautier suggested, salts of a labile hydrogen isocyanide; their relation to ordinary hydrogen cyanide or formonitrile is similar to that of the salts of Hantzsch's labile *iso*nitromethane to normal nitromethane:

$$CH_3{\cdot}NO{:}O + K{\cdot}OH = CH_3{\cdot}NO(OH){\cdot}OK = H_2O + CH_2{:}NO{\cdot}OK\ ;$$

$$H{\cdot}C{:}N + K{\cdot}OH = H{\cdot}C(OH){:}NK = H_2O + C{:}NK.$$

The labile isomeride could only be made from metallic cyanides by the action of acids. These necessarily contain electronegative radicles, and therefore combine with the carbon of the cyanide, yielding the normal or nitrilic hydrogen compound:

$$K{\cdot}N{:}C + HCl = K{\cdot}N{:}CH{\cdot}Cl = KCl + N{:}CH.$$

*45. "The absorption spectra of metallic nitrates. Part I." By W. N. Hartley, D.Sc., F.R.S.

Soret was the first to observe an absorption band in solutions of nitric acid and potassium nitrate, but Soret and Rilliet did not observe it in ethyl nitrate. The author made, in 1887, an extended examination of the absorption spectra of nitrates of the simplest constitution to see if he could find any difference corresponding to that observed by Bunsen in the salts of didymium (*Pogg. Ann.*, 1866, 128, 100).

The results obtained by the author show that the curves of nitric acid and potassium nitrate are identical, but those from silver and thallium nitrates differ widely from one another and from that of nitric acid. In the case of nitric acid, the mean position of the band primarily due to NO_3 lay between λ317 and 285. The general effect of silver nitrate is to cause an absorption of all rays beyond λ340, but there is a feeble transmission of a line about λ274. Thallium nitrate has an absorption band from λ324 to 274. With a dilution of $N/1000$, there is still an absorption of the rays about λ242, although water transmits the rays to λ211.

The solutions were examined in two ways, namely, (1) by using a fixed length of tube (200 mm.) and varying the strength of the solutions, the best results being obtained with solutions between $N/20$ and $N/200$, (2) by using normal solutions and varying the length of tube.

With normal solutions and a 200 mm. tube, nitrates of the following transmitted a strong continuous spectrum to somewhere about λ340, after which there was a complete general absorption.

H λ346	Mg λ357	Tl λ340 ($N/4$)
Li 346	Ca 340	Ba 340 ($N/4$)
Na 340	Zn 346	Pb 346 ($N/2$)
K 346		
Ag 355		

46. "A method of determining the ratio of distribution of a base between two acids." By H. M. Dawson and F. E. Grant.

The method consists in shaking up an aqueous solution containing two acids and a base (the latter being insufficient for saturation of the acids) with a second liquid which is but slightly miscible with water, and which is capable of extracting one and one only of the four substances present in the solution. Tartaric, malic, succinic, and citric acids are not extracted from their aqueous solutions by chloroform, but considerable quantities of acetic acid are.

Determinations of the ratio of distribution of acetic acid between water and chloroform at 20° have been carried out, and show that this ratio increases very considerably with the dilution. By means of a diagram on which the acetic acid concentrations are plotted as abscissæ, and the distribution coefficients as ordinates, the concentration of the acid in water corresponding to any given concentration in chloroform can be readily ascertained. The influence of the presence of the salts and the second acid on the distribution ratio of the acetic acid has been investigated and found to be small.

On shaking up an aqueous solution containing soda, acetic, and tartaric acids with chloroform and determining the concentration of the acetic acid in the latter, then from the diagram the concentration of the free acetic acid in the aqueous solution can be ascertained. If the original concentrations of the base and the two acids are known, the concentrations of the free tartaric acid and of the two salts can be calculated.

The aqueous solutions were prepared in such a manner that after shaking up with an equal volume of chloroform, the base and the two acids were present in as nearly as possible equivalent quantities, the excess of acetic acid required in the original solution being determined from the preliminary distribution experiments.

Several series of experiments have been carried out in which acetic acid is compared with the several acids above mentioned, three or four concentrations being investigated in each case, and the ratios determined for the distribution of the base between acetic and each of these acids.

This method of determining the ratio of distribution of a base between two acids can also be employed where the second liquid takes

up two of the components, for example, the two acids from the aqueous solution, but the ratios of distribution of the two acids between water and the second liquid must differ considerably from one another at any given concentration.

47. "On the molecular complexity of acetic acid in chloroform solution." By H. M. Dawson.

The considerable increase of the ratio in which acetic acid distributes itself between water and chloroform with increasing dilution is shown to be due to a gradual dissociation of the double molecules present in the latter solvent into simple molecules.

The limiting concentrations at which distribution experiments have been carried out correspond to an almost complete change in the molecular complexity of the dissolved acid. At a concentration of 12 grams per litre of chloroform, the acetic acid present in the form of double molecules is about five times as great as that in the form of simple molecules, whilst at a concentration of 0·1 gram per litre the proportion is only one-fifth.

The formation of double molecules by substances containing the hydroxyl group, when dissolved in liquids not containing this group, appears to be essentially dependent upon the concentration.

48. "On the existence of polyiodides in nitrobenzene solution." By H. M. Dawson and R. Gawler.

In the course of experiments on the ratio of distribution of iodine between potassium iodide solution and nitrobenzene, it was observed that as the amount of iodine added was continually increased, the concentration of the iodine in the aqueous layer reached a maximum value and then gradually decreased.

Further distribution experiments, made with a view of explaining this peculiar phenomenon, showed that the potassium iodide in the aqueous solution was extracted by the nitrobenzene on addition of iodine to the system. Using the same volumes of nitrobenzene and potassium iodide solution in successive experiments, the amount of potassium iodide thus extracted by addition of varying quantities of iodine was determined, and further, the influence of the amount of nitrobenzene for constant quantities of potassium iodide solution and of iodine was investigated. The removal of the potassium iodide by the nitrobenzene is probably due to the formation of polyiodides and the great solubility of the latter in nitrobenzene.

With a view of determining the nature of the polyiodides thus

formed, the solubility of potassium iodide in nitrobenzene containing different quantities of iodine has been determined. If the concentration of the iodine does not exceed 0·3 gram-molecules per litre, it is found that one molecule of potassium iodide dissolves for each molecule of iodine present, indicating the formation of the triiodide. As the concentration of the solutions thus saturated with regard to potassium iodide increases, the molecular ratio of iodine to potassium iodide gradually increases and approximates to the value two.

Determinations have also been made of the solubility of iodine in nitrobenzene containing potassium iodide. For all solutions containing more than sixty grams of potassium iodide per litre, the molecular ratio of the dissolved iodine to potassium iodide is equal to four, and there is some probability that this ratio holds for the more dilute solutions if the uncombined iodine present in the solution is taken into account. The results of this series of solubility determinations lead to the conclusion that the polyiodide KI_9 is present in the solution.

The nitrobenzene solutions have been examined with regard to their electrical conductivity, and in accordance with the high dielectric constant of nitrobenzene it is found that the solutions are good conductors. Their conductivity is approximately one-fifth that of aqueous solutions of potassium iodide of the same molecular concentration. Determinations of the freezing point of solutions of iodine in nitrobenzene, and of solutions containing in addition to iodine an equimolecular amount of potassium iodide, indicate that the triiodide is dissociated to a very considerable extent, although the difficulties of freezing point measurements with nitrobenzene as solvent prevent an accurate quantitative estimation of the degree of dissociation.

49. "Derivatives of α-aminocamphoroxime." By A. Lapworth and A. W. Harvey.

α-Aminocamphoroxime, $C_8H_{14}\begin{cases}CH\cdot NH_2\\ C{:}N\cdot OH\end{cases}$, is made by heating aminocamphor with a solution of hydroxylamine acetate in presence of a large excess of sodium acetate. It crystallises from benzene in flattened prisms or thin plates melting at 144—145° and dissolves in dilute alkalis and acids. It has $[\alpha]_D = +60{\cdot}5°$ in a 1 per cent. solution in absolute alcohol and $+36{\cdot}7°$ in dilute acids. The *hydrochloride*, $C_{10}H_{18}N_2O_2,HCl,H_2O$, forms small prisms and has $[\alpha]_D = +28{\cdot}3°$ in water. The *platinichloride*, $(C_{10}H_{19}N_2O)_2PtCl_6$, forms yellow needles melting and decomposing at 209—211°.

The *dibenzoyl* derivative, $C_8H_{14}\begin{cases}CH\cdot NH\cdot COPh\\ C{:}NO\cdot COPh\end{cases}$, crystallises in bril-

liant prisms which melt at 146—147°. In absolute alcohol $[\alpha]_D = +104{\cdot}8°$.

The *carbamide*, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CONH_2\\ C:NOH\end{matrix}$, crystallises in two forms, which appear, however, to melt and decompose at the same temperature, namely, 203—204°. It has $[\alpha]_D = +40{\cdot}9°$ in absolute alcohol.

The *benzylidene* compound, $C_8H_{14}<\begin{matrix}CH\cdot N:CHPh\\ C:NOH\end{matrix}$, prepared by the interaction of the oxime with benzaldehyde in alcoholic solution, forms brilliant, transparent, apparently hemimorphic prisms melting at 153—154°. In alcohol $[\alpha]_D = 226{\cdot}9°$.

Aminocamphoroxime unites with two molecular proportions of phenylcarbimide, forming a *compound*, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CO\cdot NHPh\\ C:N\cdot O\cdot CO\cdot NHPh\end{matrix}$, which crystallises in asbestos-like needles melting at 175—177°. In absolute alcohol $[\alpha]_D = -56{\cdot}6°$.

The products obtained by the action of heat or of dehydrating agents, such as acetyl chloride, upon aminocamphoroxime do not appear to contain any compound corresponding with the campholenonitriles.

50. "Preparation of sulphamide from ammonium amidosulphite." By E. Divers and M. Ogawa.

It has been pointed out by the authors (*Trans.*, 1900, **77**, 324) that a substance, apparently sulphamide, is one of the products of decomposition of ammonium amidosulphite. They have since proved that this substance is sulphamide, and that ammonium amidosulphite is a much better source of it than sulphuryl chloride has been found to be by Hantzsch and Holl (*Ber.*, 1901, **34**, 30). The yield is 10 per cent. or more, and it is accompanied by no substances which are difficult to remove. Ammonium amidosulphite is slowly heated to, and then maintained at, a temperature of about 70°, so as first to decompose the salt and then to destroy much of the thionic compounds which accompany the sulphamide. The product is dissolved in water and practically everything but ammonium amidosulphate separated from the sulphamide by treating the solution with barium hydroxide and with silver nitrate. With some simple precautions, necessitated by the presence of the amidosulphate, the sulphamide is precipitated as silver salt and recovered from this, almost as Traube directs.

51. "Hypoiodous acid." By R. L. Taylor.

It has been concluded by Orton and Blackman (*Trans.*, 1900, 75, 830) that "the solutions obtained from iodine and mercuric oxide contain only a small quantity of hypoiodite, and that the iodine is chiefly present as iodate." This is contrary to the results described by the author in a former paper (*Mem. Manchester Phil. Soc.*, 1897, 41, 8), where he used aqueous iodine (1 part in 5000) and obtained 80 to 90 per cent. of the possible amount of hypoiodite. He has made further experiments and finds that the proportion of iodine existing in the filtrate as hypoiodous acid increases with the fineness of division of the iodine, and diminishes as the proportion of iodine to the water employed increases and with the time occupied in shaking and filtering. Using powdered iodine, about 2 parts to 1000 of water, and occupying (as Orton and Blackman did) 15 minutes in shaking and 10 minutes in filtering, the author obtains results not very different from theirs; but using *precipitated* iodine with the same proportion of water and taking only a little over a minute in shaking and filtering, the filtered liquid contains 44 to 52 per cent. of the possible amount of iodine as hypoiodous acid, and of the total iodine in the filtered liquid 90 to 95 per cent. exists as hypoiodous acid and only 5 to 10 per cent. as iodic acid. The solution of hypoiodous acid decomposes very rapidly, beginning to turn brown, owing to the liberation of iodine, almost immediately after filtering, unless a very dilute solution of iodine has been employed. Consequently it is impossible to obtain good results unless all the operations are performed very quickly. The filtered liquid always contains a little mercury. The author has estimated this, and finds that although the hypoiodite in the filtrate may exist partly as mercuric hypoiodite, there is so little mercury present that a considerable proportion of the iodine must exist as hypoiodous acid.

52. "Synthesis of imino-ethers. *N*-aryl benzimino-ethers." By G. D. Lander.

The preparation of imino-ethers of the type Ph·COR:NPh from the imide chlorides of the corresponding benzoyl arylamines was described. The reaction between the imide chlorides and sodium alcoholates occurs most readily when the latter are employed in alcoholic solution. Intramolecular rearrangement does not take place in the formation of the methyl compounds.

N-phenylbenziminoethyl ether, $C_6H_5C(OEt):NC_6H_5$, boils at 168—170° at 14 mm.; the *methyl* compound at 157—158° at 12 mm., and the n-*propyl* ether at 177—179° at 11 mm.

As a bye-product in the syntheses of the methyl and ethyl ethers, benzoyldiphenylbenzenyl amidine, $C_6H_5C{:}NC_6H_5{\cdot}N(COC_6H_5)C_6H_5$, yellow prisms of m. p. 170—172°, was detected.

N-*o*-*tolylbenziminoethyl ether*, $C_6H_5C(OEt){:}NC_7H_7$, boils at 179—180° at 15 mm., the *methyl* ether at 173° at 15 mm.

N-p-*tolylbenziminoethyl ether* boils at 178° at 11 mm., the *methyl* ether at 177° at 12 mm.

Reference was made to the formation, by the action of acetyl chloride containing hydrochloric acid on a light petroleum solution of the base, of the hydrochloride of *N*-*o*-tolylacetiminoethyl ether, $CH_3C(OEt){:}NC_7H_7,HCl$, which is crystalline, melts at 109—110°, and decomposes into ethyl chloride and acetotoluidide. Similarly, *N-phenylacetiminoethyl ether hydrochloride*, $CH_3C(OEt){:}NC_6H_5,HCl$, m. p. 100° with decomposition, has been prepared for the first time.

***53. "Nitration of *s*-trihalogenacetanilides." By K. J. P. Orton.**

As a sequel to the author's work on the action of nitric acid on *s*-trihalogenanilines (this vol., p. 58) the nitration of *s*-tribromoacetanilide and of 4-chloro-2 : 6-dibromoacetanilide has been investigated. Remmers (*Ber.*, 1874, 7, 351) and Bentley (*Amer. Chem. Jour.*, 1898, **20**, 472) have subjected *s*-tribromoacetanilide to the action of fuming nitric acid; the former obtained an anilide, $C_6HBr_3(NO_2)NHAc$, crystallising in yellow needles from which an aniline, $C_6HBr_3(NO_2){\cdot}NH_2$, was prepared by hydrolysis with ammonia; it crystallised in yellow needles and melted at 214—215°, whilst 2 : 4 : 6-tribromo-3-nitroaniline, according to Körner (*Jahresbericht*, 1875, 347), melts at 102·5°. Bentley was unable to confirm Remmer's results.

By cautiously warming the anilides above mentioned with fuming nitric acid, the author has obtained respectively 2 : 4 : 6-tribromo-3-nitroacetanilide and 4-chloro-2 : 6-dibromo-3-nitroacetanilide. In neither case was the nitration complete; the nitrated anilide was isolated in a pure state by conversion of the mixture of anilides into the acetylchloroamino-derivatives, the latter can be readily separated by fractional crystallisation from petroleum, in which the nitrated chloroamine (for example, acetylchloroamino-2 : 4 : 6-tribromo-3-nitrobenzene) is but little soluble. By treatment with alcohol, the anilide is obtained from the pure acetylchloroamino-derivative.

The following substances have been prepared:

2 : 4 : 6-*Tribromo-3-nitroacetanilide*, $C_6HBr_3(NO_2)NHAc$, from 2 : 4 : 6-tribromo-3-nitroaniline (m. p. 102°, Körner), and by nitrating *s*-tribromoacetanilide, colourless needles, m. p. 216—217°; 2 : 4 : 6-*tribromo-3-nitrodiacetanilide*, $C_6HBr_3(NO_2){\cdot}NAc_2$, rhombs, m. p. 175—176°;

acetylchloroamino-2 : 4 : 6-*tribromo*-3-*nitrobenzene*, $C_6HBr_3(NO_2)NClAc$, prisms, m. p. 159°.

4-*Chloro*-2 : 6-*dibromo*-3-*nitroaniline*, $C_6HClBr_2(NO_2)\cdot NH_2$, prepared by brominating 4-chloro-3-nitroaniline (m. p. 103°), and by hydrolysis of the corresponding anilide, pale yellow needles, m. p. 103—104°.

4-*Chloro*-2 : 6-*dibromo*-3-*nitroacetanilide*, $C_6H\cdot ClBr_2(NO_2)\cdot NHAc$, prepared from the corresponding aniline and by nitrating 4-chloro-2 : 6-dibromoacetanilide, silky needles, m. p. 224°; *acetylchloroamino*-4-*chloro*-2 : 6-*dibromo*-3-*nitrobenzene*, $C_6HClBr_2(NO_2)\cdot NClAc$, short prisms, m. p. 134—135°.

Attention is called to the fact that, whereas in the action of nitric acid on *s*-tribromoaniline a nitroamine is first formed, which then undergoes change, the nitro-group displacing the para-bromine atom in the nucleus (this vol., p. 58), with the anilide no such displacement occurs, but only nitration in the meta-position. Acetylation, combined with the presence of two ortho-placed halogen atoms, prevents partially, at least, the amino-group from exercising its usual directing function.

54. "Purpurogallin. Preliminary Notice." By A. G. Perkin and A. B. Steven.

To purpurogallin, an oxidation product of pyrogallol, Clermont and Chautard (*Jahresbericht*, 1882, 683) assigned the formula $C_{20}H_{16}O_9$, and described a tetra-acetyl compound, $C_{20}H_{12}O_9(C_2H_3O)_4$, m. p. 186°, and a tetrabromo-derivative, $C_{20}H_{12}Br_4O_9$, m. p. 202—204°. Nietzki and Steinmann (*Ber.*, 1887, 20, 1278) preferred the formula $C_{15}H_{14}O_9$, and found that on distillation with zinc dust naphthalene is produced. This preliminary investigation, while corroborating, as a rule, the analytical numbers of these chemists, indicates that the molecular weight of purpurogallin is much lower, most probably being represented by $C_{11}H_8O_5$. The *tetra-acetyl* compound, m. p. 182—183°, $C_{11}H_4O_5(C_2H_3O)_4$, and the *tribenzoyl* compound, $C_{11}H_5O_5(C_7H_5O)_3$, minute colourless prisms, m. p. 213° (found C = 71·99; H = 3·86; molecular weight [cryoscopic] = 556), have been studied. Analyses of the *dibromo*-compound, $C_{11}H_6Br_2O_5$, m. p. 204—206° (found C = 35·10; H = 1·67), and the *monopotassium* salt, $C_{11}H_7O_5\cdot K$ (found K = 14·76) minute, brown-violet needles, point to the correctness of this formula. Hooker (*Ber.*, 1887, 20, 3260), by means of nitrous acid, obtained purpurogallin from gallic acid. If, however, potassium ferricyanide in conjunction with potassium acetate be employed, a small quantity of a new compound crystallising in minute, orange-red needles is formed,

which appears to be purpurogallin carboxylic acid, $C_{11}H_7O_5 \cdot CO_2H$ (found C = 54·56, 54·14; H = 3·73, 3·18).

55. "Quercetagetin." By A. G. Perkin.

Quercetagetin was isolated from the flowers of the African marigold (*Tagetes patula*) by Latour and Magnier de la Source (*Bull. Soc. Chim.*, 1877, **28**, 337) as a yellow, crystalline substance, $C_{27}H_{22}O_{13} + 4H_2O$. A reinvestigation indicates that its true formula is $C_{15}H_{10}O_8$ (found C = 56·66, 56·47; H = 3·25, 3·31), as it gives a *sulphate*, $C_{15}H_{10}O_8, H_2SO_4$ (found C = 43·28; H = 3·29), orange needles, and a *monopotassium* salt, $C_{15}H_9O_8K$ (found K = 10·74). Quercetagetin melts at 318—320°, gives an *acetyl* compound, $C_{15}H_4O_8(C_2H_3O)_6$ (found C = 57·37; H = 3·87; $C_{15}H_{10}O_8$ = 55·82), colourless needles, m. p. 203—205°, and dyes shades browner, though somewhat similar to quercetin, to which class of colouring matter it appears to belong. It contains no methoxyl group and on fusion with alkali gives protocatechuic acid and a phenol at present unidentified. As there is considerable difficulty in obtaining raw material, the conclusion of the investigation may be delayed for some time.

ADDITIONS TO THE LIBRARY.

I. By Donation.

Lewkowitsch, Julius. The laboratory companion to fats and oils industries. Pp. 147. London 1901. From the Author.

Lewkowitsch, Julius. Laboratoriumsbuch für die Fett- und Ölindustrie. Pp. 148. Braunschweig 1902. From the Author.

II. Purchase.

Engelhardt, Viktor. Die Elektrolyse des Wassers, ihre Durchführung und Anwendung. Pp. 117. Halle-a-S. 1902.

Hofmann, Reinhold. Ultramarin. Pp. 154. Braunschweig 1902.

III. Pamphlets.

Class list and index of the Periodical Publications in the Patent Office Library. Pp. 191. London 1902.
From the Comptroller-General of Patents.

Fowler, Gilbert J. Some points in the management of septic tanks and bacterial contact beds. Pp. 11. London. From the Author.

Tankard, Arnold R. Artificial silk (Lecture delivered before the Sheffield Microscopical Society). Pp. 15. From the Author.

ANNUAL GENERAL MEETING

The Annual General Meeting of the Society for the election of Officers and Council, and for other business, will be held on **Wednesday**, March 26th, at **half-past four** o'clock in the afternoon.

RAOULT MEMORIAL LECTURE.

The Raoult Memorial Lecture will be delivered by Professor van't Hoff, on **Wednesday**, March 26th, at **9** p.m.

This lecture will be delivered, by kind permission of the Managers, in the Theatre of the Royal Institution, 21, Albemarle Street, W.

Admission will be by ticket only. Each Fellow of the Society will be entitled to two tickets, which may be obtained on application to the Assistant Secretary, Chemical Society, Burlington House.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 25/4/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. No. 250.

March 26th, 1902. Annual General Meeting. Professor EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

Dr. HENRY and Mr. RAMAGE were appointed Scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT, in beginning his address, said that he had the agreeable duty of congratulating the Fellows on the continued and ever increasing prosperity of the Society.

The numerical strength of the Society was 2335 on March 28th, 1901. Since that date 163 Fellows had been elected, and 3 had been reinstated by the Council, making a gross total of 2501. Of these, 32 had withdrawn, 25 had been removed for non-payment of two annual subscriptions, and 21 had died.

The actual number of Fellows to date was therefore 2423, the highest number yet reached, and the number of Foreign Members was 32.

The names of those removed for non-payment of subscriptions were:—

E. W. Allsom, W. D. Bohm, C. F. Branson, T. H. Coleman, E. D. Ewen, F. G. Fuller, C. H. Field, W. G. Fraser, A. T. Gailleton, W. H. Grieve, T. C. Hepworth, A. F. Hogg, J. Harger, W. Ince, R. S. Ladell, R. D. Littlefield, D. C. Mackenzie, A. Mackay, F. L. Overend, M. Pearson, S. Smith, A. H. Turton, C. W. Vincent, W. H. Walker, A. Walton.

The following have withdrawn:—

J. M. Arnot, W. H. Barr, F. Belton, H. D. Berridge, M. Cochran, W. Collingridge, J. Craig, H. L. Dampier, M. J. R. Dunstan, G. Evans,

H. P. FitzGerald, P. H. Grant, W. H. Greene, H. W. Gough, A. B. Griffiths, J. B. Guyer, H. M. Hastings, E. S. Hayward, A. H. Macdonald, C. J. S. Makin, J. Maudsley, J. McLeod, H. C. Myers, G. A. Parkes, L. G. Patterson, J. C. Quinn, A. Schloesser, C. Thompson, E. A. Wates, J. I. Whimster, B. W. Winder, S. Wood.

The following have died :—

F. J. Beale, J. H. Beckett, Henry Bird, Sir J. H. Gilbert, F.R.S., A. Hartridge, Alexander Hay, Lawrence Hislop, David Johnson, N. Leonard, H. G. Madan, Dr. Ira Moore, Dr. G. Harris Morris, John Paul, W. Shapleigh, Louis Siebold, Prof. Maxwell Simpson, F.R.S., W. T. N. Spivey, W. Terrill, John Thomson, J. L. W. Thudichum, G. F. Wilson, F.R.S.

The most important test of the prosperity of the Society was, however, to be found in the record of its work. In this respect also he had a favourable report to make. Since the last anniversary, 181 communications had been made to the Society. Abstracts of all these had appeared in the *Proceedings*, whilst 139 had already been published in the *Transactions*. He ventured to think that the quality, generally, of the work presented was as high as in any previous year, and clearly indicated the continued enthusiasm and activity of the Fellows.

The *Transactions* for 1901 contained 146 memoirs, occupying 1411 pages; and the volume of the preceding year 127 memoirs occupying 1334 pages.

The volumes for 1901 contain 3754 abstracts of papers, published mainly in Continental journals, occupying 1496 pages, arranged as follows :

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	784	1530

PART II.

General and Physical Chemistry		403
Inorganic Chemistry		376
Mineralogical Chemistry		169
Physiological Chemistry		363
Chemistry of Vegetable Physiology and Agriculture		306
Analytical Chemistry		607
	712	2224
Total in Parts I. and II.	1496	3574

The volume for 1901 contained a Memorial Lecture giving an account of the life-work of Rammelsberg. A set of the Memorial Lectures

which had appeared up to the end of 1900 was issued in September last in a separate form.

The use of the Library by the Fellows continued to show their appreciation of it. Eight hundred and eighty books had been borrowed, as against 810 during the corresponding period of last year. A large number of these were Journals issued by post to Fellows resident in the country, and the Library Committee invited special attention to this development of the Society's usefulness. The additions to the Library comprised 153 books, 441 volumes of periodicals, and 33 pamphlets as against 95 books, 327 volumes of periodicals, and 30 pamphlets during the corresponding period of last year.

It was desirable that the Society should have in the Library a copy of, at least, every work printed in English on chemical subjects to the end of the 18th century, and he would invite the co-operation of the Fellows in making the Library complete in this direction.

In the preparation of the new Library catalogue, the printing of which had been decided upon, advantage was taken of the opportunity to construct a new and convenient Card Catalogue, which, it was believed, would materially assist readers in making use of the Library.

It was his privilege to offer, on behalf of the Society, its warm congratulations to Dr. Schunck, to Mr. Lloyd Bullock, and to Dr. Francis, who this year have reached their sixtieth anniversary of admission to the Fellowship of the Society. He had pleasure to add that Mr. Buckton, F.R.S., Mr. F. Claudet, and Mr. Darby have reached their jubilee, and to them he would also convey its sincere congratulations.

Last year their illustrious senior Foreign Fellow, M. Berthelot, celebrated the fiftieth anniversary of his first scientific publication, and all countries united in expressing their admiration and respect for the veteran chemist. On behalf of the Society, he, with Dr. Gladstone and Professor Ramsay, presented a congratulatory address to M. Berthelot at the imposing function which was held in the Sorbonne on November 24th, 1901. This address had already been printed in the *Proceedings*.

During the year, the Society had joined in the celebration of the 450th anniversary of Glasgow University, and in the jubilee of Owens College, Manchester.

Considering the large number of Fellows now in the Society, the mortality is small; nevertheless, this year they had to regret the loss of 21 Fellows. This melancholy list includes the name of Sir Henry Gilbert, Past President of this Society, and one ever devoted to its welfare. His immense work, carried out with Sir John Lawes, laid the scientific foundation of British Agriculture and serves as the model on which all future researches must proceed. The Society was fully represented on the sad occasion when Sir Henry Gilbert was interred,

and its representatives laid a wreath on his grave, while later on the Council passed a vote of condolence with his mourning relatives. In a short time, he hoped, a full obituary notice would be published by one far more competent to undertake it than he. Dr. Maxwell Simpson is another of those passed away from amongst us, full of years, leaving memories of good work well done, especially in synthetic chemistry, and of him and of the other Fellows whose life-work has closed records will also be shortly published.

Considerable discussion had taken place within the Society on the question of altering the day and hour of the Ordinary Meetings, which was raised in the address of his predecessor, Dr. Thorpe, last year. They had had two Extraordinary Meetings on this subject, and the outcome was the experiment now in operation, of trying alternate evening and afternoon Meetings until the end of the present session. Until that experiment had been fairly made, the best course, obviously, was to suspend judgment on the question.

Grants amounting to £250 had been made from the Research Fund in aid of chemical investigations.

The remainder of the address dealt with certain aspects of the periodic law as modified by recent discovery.

Dr. GLADSTONE, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the *Transactions*.

Dr. THORPE, C.B., F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks,

Prof. TILDEN, F.R.S., the Treasurer, in giving an account of the Balance Sheet which he laid before the Society, duly audited, said :—

The receipts had been :—By admission fees and subscriptions, £4532 ; by sale of Journal and advertisements, £835 11*s.* 2*d.* ; and by dividends on invested capital, £476 12*s.* 6*d.* The total receipts from all sources amounted to £5884 1*s.* 8*d.* The expenses had been : —On account of the Journal, £3233 0*s.* 2*d.* ; on account of the Proceedings, £20 1*s.* 5*d.* ; on account of the Library Catalogue, £42 14*s.* 4*d.* ; on account of the Library, £429 15*s.* 5*d.* ; House expenses, £239 19*s.* 1*d.* ; the total expenditure being £4913 10*s.* 6*d.*

The TREASURER, in concluding, proposed a vote of thanks to the auditors, which was acknowledged by Mr. CHAPMAN.

Prof. H. B. DIXON, F.R.S., proposed a vote of thanks to the Treasurer, Secretaries, and Council.

Dr. HEWITT seconded the motion, which was unanimously adopted. Prof. MELDOLA, F.R.S., responded.

The Scrutators having presented their report to the President, he declared that the following had been duly elected :—

President: J. Emerson Reynolds, Sc.D., M.D., V.P.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; J. Dewar, M.A., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., LL.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: E. Divers, M.D., D.Sc., F.R.S.; P. F. Frankland, LL.D., F.R.S.; H. McLeod, F.R.S.; R. Meldola, F.R.S.; H. A. Miers, D.Sc., F.R.S.; T. Stevenson, M.D.

Secretaries: W. R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary: W. Ramsay, LL.D., F.R.S.

Treasurer: W. A. Tilden, D.Sc., F.R.S.

Other Members of Council: H. B. Baker, M.A.; F. D. Chattaway, Ph.D., D.Sc.; F. Clowes, D.Sc.; J. J. Dobbie, M.A., D.Sc.; A. E. Dixon, M.D.; M. O. Forster, Ph.D., D.Sc.; A. Harden, M.Sc., Ph.D.; J. Lewkowitsch, Ph.D.; J. E. Marsh, M.A.; S. U. Pickering, M.A., F.R.S.; J. A. Voelcker, Ph.D.; J. Walker, D.Sc., F.R.S.

March 26th, 1902. Extra Meeting. Professor Emerson Reynolds, Sc.D., V.P.R.S., President, in the Chair. This meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

Professor J. H. van't Hoff, F.R.S., delivered the Raoult Memorial Lecture.

François Marie Raoult was born on May 10th, 1830, at Fournes, in the Department of Nord. When he went to Paris to pursue his studies he had neither fortune nor patronage to assist him, so had to struggle to find means to keep himself. His first paper, published in 1853, contained observations on the transport of electrolytes by the galvanic current and on electrical endosmosis. In 1853 he was

appointed "Aspirant repétiteur" in the Rheims Lycée, in 1855 "Régent de Physique" in the college at St. Dié, after which he was again at Rheims, and in 1860 at Bar-le-Duc, employing his spare time in working for his degree of *Licencié ès-Sciences physiques*. In 1862, he proceeded to Sens, where, amidst adverse material surroundings, he prepared his thesis on Electromotive Force, for which in 1863 he obtained in Paris the degree of *Docteur ès-Sciences physiques*.

The work of Raoult may be divided into three distinct parts: the physical, the chemical, and the physico-chemical. His career as a physicist begins with the thesis above referred to, by which he was marked out as an accurate and independent investigator already in advance of his time by the conclusions he based on a careful examination of facts. In the first part of this research he measured and compared in the cells of the Daniell type the amount of heat due to the chemical action with that corresponding to the electrical work produced, and showed that they were by no means identical. The second part was devoted to the decompositions in the voltameter by the galvanic current, the thermal phenomena being especially studied. It was whilst carrying out his electro- and thermo-chemical investigations that Raoult entered the *Faculté des Sciences de Grenoble* in 1867 as "chargé du cours de Chimie," being promoted in 1870 to the Chair of Chemistry, which he occupied until his death last year.

From this time forward a change is visible in the direction of Raoult's work, which now became of a more purely chemical kind, the problems still being looked at from the physical point of view. These problems included the examination of the gas from a "fontaine ardente," which he showed to be merely methane, the proof of presence of copper and zinc as normal constituents of the human liver, the inverting action of light on sugar. He showed that the presence of carbon dioxide in air diminished the production of carbon dioxide in the lungs, but that this effect was counteracted by the increased pulmonary action. His discovery of a basic calcium carbonate, $CaCO_3,CaO$, which acts like plaster of Paris on the addition of water, formed the subject of his last purely chemical paper. After this, he definitely enters upon that line of research which he has made peculiarly his own, and in which he persevered until his death.

His first paper on freezing points was published in 1878 and was of a purely empirical nature, pointing out the proportionality existing between the lowering of the freezing point and that of vapour pressure (or raising of boiling point). Probably owing to the difficulty of determining the strength of alcoholic liquors by means of their vapour pressures or boiling points, he tried their freezing points. How this was related to practical applications is shown by the table appended to the paper, the liquids beginning with cider and ending

with Marsala, the freezing points varying from $-2°$ to $-10·1°$, and corresponding fairly with the proportion of alcohol. From solutions of ethyl alcohol he passed to those of other alcohols, and thence to other organic compounds, giving his well known table relating to twenty-nine substances. His conclusion was that the product of the depression of freezing point of a solution containing 1 gram of substance in 100 grams of water multiplied by the molecular weight of the dissolved substance is a constant. Two further papers in 1882 extended the freezing point law to solvents other than water, and he showed that each solvent has its own molecular constant which, probably by the formation of double molecules of the dissolved substance, may be reduced to half the normal value. This constant is proportional to the molecular weight of the solvent (M_1) and is on an average $\frac{K}{M_1} = 0·62$. From organic compounds he passed to the more difficult cases of salt solutions, beginning with those of acids and bases and finding that strong monobasic acids like hydrochloric acid and strong mono-acid bases like potassium hydroxide have a molecular depression of 37 whilst the weaker ones, like organic compounds, have only 18·5. He summed up his results thus: "These facts prove that, in opposition to what I had admitted up till now, the general law does not apply to dissolved salts; on the contrary they tend to indicate that it is applicable to the constituent radicles of the salts, almost as if these radicles were simply mixed in the solutions."

The early work of Raoult on voltaic cells was neglected, as it was much before its time, but his work on cryoscopy appeared just in the nick of time and was soon warmly received everywhere. In 1892 he again took up his study of freezing points which had been interrupted in 1884, but now from the point of view of the new theory of solutions, and showed that the molecular depressions of potassium chloride and sugar, as well as of sodium chloride and alcohol, were in accordance with the hypothesis of Arrhenius. In his summary of work in this direction, Raoult admitted all the conclusions of the theory of solutions, but as a thoroughly experimental investigator he objected to build upon that large but hypothetical generalisation known as the extended Law of Avogadro.

The relations existing between lowering of freezing point and of vapour pressure led Raoult to his tonometric work. He found (as Wüllner had already proved in some cases) that the ratio existing between the lowering of the pressure ($f-f'$), and the pressure itself (f), namely, $\frac{f-f'}{f}$, the so-called *relative lowering* of pressure was independent of the temperature. His next step was to determine the

values of the *molecular relative lowering*. He thus formulated what he found: "One molecule of a non-volatile substance (salts excepted) dissolving in 100 molecules of any volatile liquid, diminishes the vapour pressure of that liquid by an almost constant fraction of its value, which is about 1·05 per cent." This conclusion at once brought him into connection with the theory of solutions, and Raoult himself says of it, in 1887, that "the agreement between experiment and theory is thus in all respects as complete as one can desire in such matters." In 1893, along with Recoura, he gave his most general and exact expression of the results of his vapour pressure observations.

Raoult's constitution seems to have been a vigorous one, the only indication to the contrary being his resignation, in 1892, of an additional professorship which he had held. He ought to have retired in April, 1900, on account of his having reached the age limit for the tenure of his chair, but by special decision of the Trustees he remained in office "hors cadre," a very high honour, and a proof of his unbroken vigour at that time. In his last year, in two comprehensive papers, he summed up his views on Tonometry and on Cryoscopy; it was just in time, for, with practically no premonitory symptoms, he died on April 1st, 1901.

His character as a man may be read in his papers, in which he showed activity, patience, tenacity in pursuing an aim, as much eye for detail as for the vaster horizon, absolute independence of mind, criticising or admitting without bias views of others as well as his own, and testing both with the same calm conviction that the last word must rest with experiment.

Prof. ODLING in proposing a vote of thanks to Prof. van't Hoff, said that he would not add a word to the appreciative, unaffected, and simple account of the work of Raoult. It was so lucid and complete that coming from any one it would have been of great interest, but in this case, coming from Prof. van't Hoff, it gave all the greater pleasure. Prof. van't Hoff's work in inorganic chemistry had exercised a very great influence on modern chemical doctrine for a quarter of a century; his work had excited a high degree of interest amongst English chemists, and to-night he had supplemented their acquaintance with his work by giving them the opportunity of making acquaintance with himself. The early work of Prof. van't Hoff did not, and very properly so, win its way without some opposition, which in certain continental schools was unduly harsh. As with his theory of the chemical atom in space, so is it with the doctrine of osmotic pressure and the philosophy of solution. He could assure Prof. van't Hoff that in no country had these been received with greater favour than in this, in spite of opposition more vivacious than weighty. They were accepted if not as

the final truth, if the truth at all, at any rate as running on all fours with the truth.

The vote of thanks was seconded by Prof. DEWAR, and supported by Sir WILLIAM HUGGINS, President of the Royal Society.

Thursday, April 17th, 1902. Professor TILDEN, D.Sc., F.R.S., Treasurer, in the Chair.

Messrs. Davis, Dorée, Aders Plimmer, Allworthy, and Bedwell were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs:
Clough, William Thomas, 3, Watford Villas, Battersea Park, S.W.
Davis, Henry Wilson, 18, Crescent Road, Kingston Hill, Surrey.
Hallowell, Thomas Butterworth, New Mills, Derbyshire.
Lessner, Charles B., 46, Broadfield Road, Hither Green, S.E.
Moore, Thomas Henry, 19, Sandmere Road, Clapham, S.W.
Rây, Prafulla Chandra, Calcutta, India.
Skertchly, William Pearson, 11, Billiter Square, E.C.
Stewart, Hector, 479, Collins Street, Melbourne.
Wells, William John, Springburn, Blackburn.
West, Joseph, 50, Poplar Grove, Fenton, Stoke-on-Trent.

Of the following papers those marked * were read :—

*56. "Dimercurammonium nitrite and its haloid derivatives." By P. C. Rây.

Some account has already been given (*Proc.*, 1901, 17, 96) of the investigation which is here more fully and accurately described. Mercurous nitrite partly decomposes in dissolving in water, giving metallic mercury and a solution of both mercuric and mercurous nitrites (*Trans.*, 1897, 71, 337). Adding to this solution just enough sodium chloride and filtering, there is left a solution of mercuric sodium nitrite, which gives, with excess of ammonia, a white precipitate of a new salt, $2NHg_2NO_2,H_2O$, dimercurammonium nitrite. On dissolving it in hydrochloric acid and evaporating, there is left a new mercuric ammonium chloride, $2HgCl_2,NH_4Cl$, a white, crystalline, volatile, and fusible salt. The corresponding bromide can be obtained in a similar way, as well as by evaporating a hydrobromic acid solution of the single bromides in the right proportions; it is largely decomposed by water into its component salts. With potassium hydroxide, not in excess, these double salts give dimercurammonium chloride

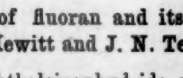
and bromide, $2NHg_2Cl,HgCl_2$, and $2NHg_2Br,HgBr_2$, the former not quite pure. With excess of potassium hydroxide, they yield the half-hydrated dimercurammonium chloride and bromide, $2NHg_2Cl,H_2O$ and $2NHg_2Br,H_2O$, the former already described by André.

When either dimercurammonium chloride or bromide is dissolved in hydrobromic acid, the above-formulated mercuric ammonium bromide is obtained on evaporation; when dimercurammonium bromide is dissolved in hydrochloric acid, a mercuric ammonium chlorobromide, $2HgCl_2NH_4Br$, is left on evaporation. From this chlorobromide, potassium hydroxide reproduces quantitatively dimercurammonium bromide, a fact which led the author at first to regard the chlorobromide as dimercurammonium bromide in union with 4 molecules of hydrochloric acid, and the corresponding double chloride and double bromide as $NHg_2Cl,4HCl$, and $NHg_2Br,4HBr$, respectively.

The author considers that the chemical composition of dimercurammonium nitrite and its derivatives gives much support to the Rammelsberg-Pesci theory of the dimercurammonium constitution of all ammoniated mercury salts.

***57. "Preparation and properties of 4-*iso*propyldihydroresorcin. A correction." By A. W. Crossley.**

The nomenclature adopted in the preliminary notice of this work (*Proc.*, 1901, 17, 172) has been changed. The substance there spoken of as 2 : 6-diketo-4-*iso*propylhexamethylene is now called 4-iso*propyldihydroresorcin*, for though this and other similar substituted dihydroresorcins behave as diketones towards hydroxylamine, there can be no doubt that their most usual form is the keto-enol modification represented by the following formula:



***58. "Oxonium salts of fluoran and its derivatives." By J. T. Hewitt and J. N. Tervet.**

Fluoran (the phenolphthaleinanhydride of Baeyer) and some of its derivatives have been examined as to their power of forming salts with strong mineral acids. The following salts have been prepared and examined: *Fluoran nitrate*, $C_{20}H_{12}O_3,HNO_3$; *monosulphate*, $C_{20}H_{12}O_3,H_2SO_4$; *dimethylfluoran nitrate*, $C_{22}H_{16}O_3,HNO_3$; *dimethylfluoran monosulphate*, $C_{22}H_{16}O_3,H_2SO_4$; *dimethylfluoran disulphate*, $C_{22}H_{16}O_3,2H_2SO_4$; *fluorescein hydrochloride*, $C_{20}H_{12}O_5,HCl$; *fluorescein monosulphate*, $C_{20}H_{12}O_5,H_2SO_4$; *fluorescein disulphate*, $C_{20}H_{12}O_5,2H_2SO_4$.

***59. "Influence of substitution on the reactivity of the aromatic metadiamines." By G. T. Morgan, D.Sc.**

The successive introduction of methyl groups into the three positions adjacent to the nitrogen atoms of *m*-phenylenediamine is attended by a well-marked diminution in the reactivity of the diamine towards methylating agents, the action of methyl chloride or bromide being prevented when the substitution of the three hydrogen atoms is complete.

m-Tolylenediamine (2 : 4-diaminotoluene), like *m*-phenylenediamine, gives rise to a mixture of tertiary base and quaternary salt; 4 : 6-diamino-*m*-xylene yields the tertiary base as the sole product, whilst diaminomesitylene is not affected.

These results agree with those obtained by Pinnow (*Ber.*, 1897, **30**, 3110; 1899, **32**, 1401; 1901, **34**, 1129), and also by E. Fischer and Windaus (*Ber.*, 1900, **33**, 345 and 1967).

The tertiary diamines containing one free para-ortho-position with respect to nitrogen are very reactive substances, darkening on exposure, yielding unstable platinichlorides, and interacting readily with formaldehyde and the diazonium salts.

4 : 6-*Tetramethyldiamino*-m-*xylene*, which contains methyl groups in each of the para-ortho-positions, is a comparatively inert substance which is not darkened by exposure to light or air; its *platinichloride* is stable, and the base itself does not condense either with formaldehyde or diazonium salts. This diamine boils at 243—245° under 757 mm., and at 124—125° under 12 mm. pressure; its *picrate* crystallises in yellow prisms melting when suddenly heated at 202—203°, but decomposing at 193—195° when maintained at this temperature for some time.

2 : 4-*Tetramethyldiaminotoluene* is a pale brownish-yellow oil boiling at 254—256° under 757 mm., and at 148—150° under 24—26 mm. pressure; its sp. gr. is 0·9661 at 24°; its *platinichloride* is decomposed by hot water; the *picrate* crystallises from alcohol in yellow prisms melting at 162—163°. The *methobromide*, $NMe_2 \cdot C_6H_3(CH_3)NMe_3 \cdot Br$, produced together with the tertiary diamine in the methylation of *m*-tolylenediamine, yields a *platinichloride*,

$$NMe_2 \cdot C_6H_3(CH_3)NMe_3, HPtCl_6,$$

crystallising in brownish-yellow scales.

p-*Nitrobenzene*-5-*azo*-2 : 4-*tetramethyldiaminotoluene*, resulting from the action of *p*-nitrobenzenediazonium chloride on 2 : 4-tetramethyldiaminotoluene, crystallises from alcohol or ethyl acetate in dark green leaflets with a bronze reflex and melts at 126—127°.

2 : 4 : 2′ : 4′-*Octamethyltetraminoditolyl*-5 : 5′-*methane*, prepared by con-

densing 2 : 4-tetramethyldiaminotoluene with formaldehyde, crystallises from alcohol in colourless prisms melting at 86°; its *picrate* separates in spherical aggregates of yellow crystals and melts at 147—148°.

60. "The influence of certain acidic oxides on the specific rotations of lactic acid and potassium lactate." By G. G. Henderson and D. Prentice, Ph.D.

The authors have examined the influence of antimonious, arsenious, and boric oxides on the rotations of aqueous solutions of potassium lactate and lactic acid, with the object of ascertaining whether any compounds of the tartar emetic type are formed in solution by interaction of these substances.

It was found that antimonious oxide is almost insoluble in solutions of potassium lactate, and that the rotations of the solutions are not appreciably affected by the presence of traces of antimonious oxide. Arsenious oxide and boric acid, on the other hand, were found to dissolve readily in aqueous solutions of potassium lactate and lactic acid. The rotations of the solutions are altered by the presence of the dissolved oxide, and in each case the maximum change occurs when the substances are present in the proportions requisite for the formation of an arseniolactate, $(AsO)C_3H_4O_3K$, and a borolactate, $(BO)C_3H_4O_3K$, respectively. The rotation of a solution of lactic acid is slightly diminished when arsenious oxide is dissolved in it, but considerably increased by the presence of boric acid.

Experiments with molybdic and other oxides are in progress.

61. "The amounts of nitrogen as ammonia and as nitric acid, and of chlorine in the rain-water collected at Rothamsted. A report to the Lawes Trust Committee." By N. H. J. Miller.

Results of monthly determinations of nitrogen as ammonia and as nitrates in the rain-water collected during thirteen harvest years (September 1888 to August 1901) at Rothamsted, showed that the total nitrogen in these forms varied from 3·31 lbs. to 4·43 lbs. per acre per annum. The average amounts for the winter and summer months, and for the whole year, are as follows:

		Nitrogen per million		Nitrogen per acre (lbs.)		
	Rainfall (inches).	as ammonia.	as nitrates.	as ammonia.	as nitrates.	Total.
Winter	14·32	0·381	0.175	1·233	0·568	1·801
Summer	12·93	0·506	0·191	1·479	0·560	2·039
Year	27·25	0·440	0·183	2·712	1·128	3·840

Of the total nitrogen 70 per cent. is present as ammonia and 30 per cent. as nitrates. During the summer months there is an increased production of ammonia, whilst the amount of nitric nitrogen (per acre) is nearly the same in summer as in winter.

Chlorine has been determined monthly for twenty-four years. The average amounts are as follows:

September 1877 to August 1901.	Rainfall (inches).	Chlorine per million.	Chlorine per acre (lbs.)
Winter months.....	14·65	3·05	10·12
Summer months	14·13	1·49	4·75
Year	28·78	2·28	14·87

The yearly amounts of chlorine in the rain vary considerably (maximum 21·19, minimum 10·32 lbs. per acre). The variations depend less on the total rainfall for the year than on the amount of rain during the winter months.

The rain falling at Rothamsted supplies, not only sufficient chlorine, but also enough sulphuric acid for the requirements of most crops.

62. "The amounts of nitrogen, as nitrates, and chlorine in the drainage through uncropped and unmanured land. A report to the Lawes Trust Committee." By N. H. J. Miller

The percolation through the 20, 40, and 60 inches of soil in the three Barnfield drain gauges amounted during 24 harvest years, Sept. 1877 to Aug. 1901, to 14·39, 15·30, and 14·41 inches per annum, being 50·0, 53·2, and 50·1 per cent. respectively of the rainfall for the same period. The maximum and minimum drainage occur in November and June.

The average loss of nitrogen, as nitrates, in the drainage is more than 30 lbs. per acre per annum, and about half of this loss takes place during October, November, and December. The yearly losses of nitrogen differ widely, according to the amount and distribution of the rain and drainage. This makes it difficult to form a decided opinion as to whether nitrification is less active at the present time than in earlier years. A very decided falling off is perhaps not to be expected in the near future. The soil of the 20-inch gauge is estimated to have contained, in 1870, as much as 6000 lbs. of nitrogen per acre, and of this amount only about 15 per cent. has been found in the drainage; in the case of the 60-inch gauge, the estimated loss is only 6·5 per cent. of the total initial nitrogen of the soil. In addition to loss of nitrogen, there is, however, a considerable loss of lime, amounting to 11 lbs. per acre (or about 20 lbs. of calcium carbonate) per inch of drainage, and this loss may, as time goes on, be expected to influence the changes in the organic matter of the soils.

The average yearly amounts of chlorine per acre in the drainage is very similar to the amount found in the rain, but wide differences occur in some individual years. In the 24 years during which the chlorine has been determined, the soils of the 20-inch and 40-inch gauges have received from the rain 7·0 and 14·4 lbs. of chlorine per acre in excess of the amounts lost in drainage. The 40-inch gauge has lost 17·5 lbs. of chlorine.

63. "Benzylidenecamphoroxime." By M. O. Forster.

An examination of α-aminocamphoroxime, described by Lapworth and Harvey (this vol., p. 70), appears to have been undertaken with the object of investigating changes which substituted camphoroximes undergo in virtue of the presence of the oximido-group. This has been the author's aim in his study of camphoroxime, which has extended over several years, and contributions to the chemistry of β-chlorocamphoroxime, β-bromocamphoroxime, and α-benzylidenecamphoroxime have been already made. As Lapworth and Harvey have notified privately their intention to abandon the investigation, the author wishes to intimate that he proposes to continue the study of substituted camphoroximes. The following observations relating to benzylidenecamphoroxime are now put on record.

Benzylidenecamphoroxime, $C_{17}H_{21}ON$, dissolves sparingly in boiling alcohol, and crystallises in transparent hexagonal prisms, melting at 197°; for a 2 per cent. solution in chloroform, $[\alpha]_D = +389°$. The *benzoyl* derivative crystallises from petroleum in lustrous, well-formed prisms, and melts at 106—107°; for a 2 per cent. solution in chloroform, $[\alpha]_D = +246°$. The *phenylcarbamate* separates from alcohol in tufts of long, silky needles, and melts at 169°, when it evolves gas; a 2 per cent. solution in chloroform has $[\alpha]_D = +275°$. Nitrous acid converts benzylidenecamphoroxime into the *compound*, $C_{17}H_{20}O_2N_2$, which melts at 117°, and gives Liebermann's reaction.

Attempts to convert the oxime into benzylidenecampholenonitrile by the agency of boiling sulphuric acid (25 per cent.) have been unsuccessful, but acetyl chloride gives rise to a *nitrile* which is unsaturated, and feebly lævorotatory.

The oxime is indifferent towards sodium amalgam, which reduces benzylidenecamphor to benzylcamphor, but sodium in boiling amyl alcohol reduces it to bases which probably represent the α-benzyl derivatives of bornylamine and neobornylamine; the *platinichloride* from the dextrorotatory hydrochloride melts at 235°, whilst the *platinichloride* from the lævorotatory hydrochloride melts at 247°.

ADDITIONS TO THE LIBRARY.

I. *By Donation.*

Simmance, John F. Calorimetry of producer and illuminating gases, with special reference to future legislation. Pp. 30. London 1902. From the Author

II. *By Purchase.*

Daniel, J. Dictionnaire des matières explosives. Préface de M. Berthelot. Pp. 815. Paris 1902.

Landolt, Hans Heinrich. Das optische Drehungsvermögen organischer Substanzen und dessen praktische Anwendungen. Zweite gänzlich umgearbeitete Auflage. Pp. 655. Braunschweig 1898.

At the next meeting, on **Wednesday, April 30th**, at **5.30 p.m.**, there will be a ballot for the election of Fellows and the following papers will be communicated :—

"On the preparation of absolute alcohol from strong spirit." By S. Young.

"On the properties of mixtures of the lower alcohols with water." By S. Young and E. C. Fortey.

"On the properties of mixtures of the lower alcohols with benzene, and with benzene and water." By S. Young and E. C. Fortey.

"Fractional distillation as a method of quantitative analysis." By S. Young and E. C. Fortey.

"On the vapour pressures and boiling points of mixed liquids. Part I." By S. Young.

"The correction of the boiling points of liquids from observed to normal pressure." By S. Young.

"Vapour pressures and specific volumes of *iso*propyl *iso*butyrate." By S. Young and E. C. Fortey.

"Nitrogen bromides containing the propionyl group." By F. D. Chattaway.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Wednesday, April 30th, 1902.

Ashe, James Samuel,
The Adelaide Hospital, Dublin.

Professor and Lecturer on Materia Medica Pharmaceutical Society, Ireland. Licentiate (1st place) and Member Pharmaceutical Society, Ireland. Late Assistant and Demonstrater Materia Medica, R.C.S.I. 1st place Honoursman Chemistry, Physics, &c., Royal College Physicians and Surgeons, Ireland. Studied Chemistry under Professor Reynolds at Dublin University.

J. Emerson Reynolds.	E. S. Cameron.
Chas. R. C. Tichborne.	John Attfield.
Thomas Tyrer.	Emil A. Werner.

Baker, Frederic Guy Stirling,
Marryatts Lodge, Snaresbrook, Essex.

Student. Studied Chemistry for four years at Oxford University, Third Class Honours in Natural Science School. At present studying Applied Chemistry in the Laboratory of Mr. Chapman.

Alfred C. Chapman.	V. H. Veley.
W. W. Fisher.	John Watts.

J. E. Marsh.

Bergtheil, Cyril,
"Checkley," Redhill, Surrey (probably removing shortly to India).

Bacteriologist. Six months at Industrie Schule, Nürnberg. Two years at University College, London. One year at South-Eastern Agric. Coll., Wye. Bacteriologist to Bihar Planters' Assoc.

William Ramsay.	A. D. Hall.
Horace T. Brown.	Morris W. Travers.

F. G. Donnan.

Boardman, Ernest, B.Sc.,

41, Knowsley Road, Smithills, Bolton.

Science Master, Central School, Bolton. Student for three years in the Owens College Laboratories. B.Sc. Vict., 1896. Five years' Science Teaching.

Harold B. Dixon. G. H. Bailey.
W. H. Perkin, jun. Norman Smith.
William A. Bone.

Blenkinsop, Richard,

Garden Wharf, Battersea.

Manufacturing Chemist. Two years at the Central Technical College under Prof. Armstrong. At present in the employ of Messrs. May and Baker, Ltd., of the above address.

Henry E. Armstrong. W. N. Hartley.
Gerald T. Moody. *David Howard.*
William A. Davis. *George Beilby.*

Bruce, Alexander,

10, Portland Terrace, Plumstead, S.E.

Chemist. Four years Assistant to Prof. Aitken, Royal (Dick) Vet. College, Edinburgh. Three years Edin. University, graduated B.Sc. 1900. Honours in Chemistry. One year Assistant Chemist Explosives Committee, Royal Arsenal, Woolwich.

Alex. Crum Brown. Hugh Marshall.
Leonard Dobbie. O. Silberrad.
William H. Sodeau.

Carrodus, Fred,

Glen Fern Tower, Lansdowne Road, Wimbledon, S.W.

Senior Science Master, King's College School, Wimbledon Common, S.W. Associate in Chemistry, Royal College of Science, 1887. Assistant Demonstrator in Physics, R.C.S., London. Assistant Lecturer in Physics, Yorkshire College, 1891—5. Extension Lecturer in Photography, Leeds, 1891—5. Senior Science Master, King's College School, Wimbledon Common, S.W., 1895—1902. House Master, King's College School, 1900—2.

John M. Thomson. Patrick H. Kirkaldy.
Herbert Jackson. Chapman Jones.
G. S. Newth.

Clowes, George Henry Alexander, Ph.D. Göttingen,

Gratwick Research Laboratory for Cancer, Buffalo, U.S.A.

Research Chemist. Student in Chemistry at Royal College of

Science, 1894—97; University of Göttingen, 1897—99; and Pasteur Institute, 1899—1900.

William A. Tilden. M. O. Forster.
W. Palmer Wynne. G. T. Morgan.
H. Burrows.

Cook, Arthur James,

167, Richmond Road, Hackney, N.E.

Appointed Assistant Chemist to the Associated Portland Cement Manufacturers, Limited. I have successfully taken the Diploma Course in Chemistry at the Central Technical College, 1898—1901.

Henry E. Armstrong. Gerald T. Moody.
T. M. Lowry. William A. Davis.
James Moir.

Crocker, James Codrington,

2, Flynone Villas, Swansea.

Junior Demonstrator, University Lab.; engaged in Research. 1st Class Nat. Science Tripos; Part I. 1900, 1st Class Nat. Science Tripos; Part II., 1901 (Chemistry). Scholar of St. John's College. B.A. (Cantab.)

G. D. Liveing. W. J. Sell.
H. J. H. Fenton. H. O. Jones.
W. H. Mills.

Crookes, Henry,

109, Ladbroke Grove, London, W.

Analytical and Metallurgical Chemist. Associate of the Royal School of Mines, Chief Assistant at the London Water Company's Laboratory for nine years, am still there. Was one year an assistant at "Cocquerel's Chemical Manure Factory" near Paris; also studied Chemistry at the "Ecóle de Médicine" at Paris, under the late Prof. Würtz.

William Crookes. James Dewar.
Henry E. Armstrong. T. E. Thorpe.
J. H. Gladstone. W. J. Russell.
David A. Louis.

Davis, Charles Benson,

218, W. 134th St., New York City, U.S.A.

Analytical and Technical Chemist. Specialist in Brewing and Bacteriology. With Dr. Durand Woodman, 80, Beaver St., N.Y., three years, as Analytical Chemist. For the past five years, and at present, Analytical Chemist to the National Brewers' Academy (Dr.

Wyatt). Papers published: 1. Water in Oils, Fats, and Waxes (*J.* [*Amer.*] *Chem. Soc.*, July, 1901). 2. New Alkalimeter, and Method for Carbonic Acid Estimation (January, 1902).

John S. Adriance. John A. Mathews.
J. H. Wainwright. *Peter T. Austen.*
W. D. Crumbie.

Everitt, Walter,

83, The Grove, Ealing, W.

Chemical Assistant at the Government Laboratory (Customs Branch). Formerly Assistant to Edward Riley, Esq.

T. E. Thorpe. James Connah.
Otto Hehner. W. Williamson.
Bernard Dyer. Edw. Riley.

Gill, J. Arthur,

19, Burma Road, Stoke Newington, N.

Analytical and Research Chemist to Messrs. A. Boake, Roberts & Co., Chemical Manufacturers, Stratford, E. Three years' chemical course at The Owens College, Manchester. Microbiology under Professor Delépine, Owens College; and Alfred Jórgensen in Copenhagen. A year of commercial analysis in the Manchester Chamber of Commerce Testing House.

B. E. R. Newlands. H. B. Dixon.
F. G. Adair Roberts. W. H. Perkin, jun.
J. F. Thorpe.

Griffiths, John T.,

Grammar School, Hanley Castle, Worcester.

Science Master. Science Master for one year at Grammar School, Pincader, Wales. Science Master for two years at Hanley Castle Grammar School, Worcester. Have taken Int. B.Sc. (Lond.), 1898. Received my training at Univ. Coll., Aberystwyth, and Royal College of Science, London.

H. Lloyd Snape. W. Palmer Wynne.
William A. Tilden. M. O. Forster.
Cecil Cooke Duncan.

Gunn, Gilbert,

209, Rochdale Road, Bury, Lancashire.

Technical Chemist in Paper Mill, thirteen and a half years. Obtained Honorary Certificate for distinguished excellence in Theoretical and Experimental Chemistry, Glasgow Royal Infirmary School of Medicine, 1883–1884. Demonstrator two Sessions, 1884–1885, 1885–1886.

Head Assistant to Professor Milne, Ph.D., F.I.C., 1887. Have investigated the Microchemical Reactions of the Celluloses.

Herbert W. Hart. A. Humboldt Sexton.
Jul. Hübner. *C. F. Cross.*
G. G. Henderson.

Hopwood, Arthur,
49, Stanley Street, Tunstall.

Science Master. Consulting and Analytical Chemist, Associate of the Royal College of Science, London. City and Guilds First Class Honours, Medallist and Prizeman in Chem. Tech. Board of Education Double Honoursman in Org. and Inorg. Chemistry. Headmaster and Lecturer on Chemistry at the School of Science, Tunstall.

George George. William Carter.
Chapman Jones. Albert Taylor.
Gerald G. Quinn.

King, Frank Eustace,
Woodbury, Polworth Road, Streatham, S.W.

Assistant Analyst. Educated at Dulwich College. Four years on Science Side; 2 years Student at University College, London Bachelor of Science of London University (First Class Hons. Chemistry); now (and for 3 years) Assistant to Dr. Bernard Dyer.

H. Brereton Baker. William Ramsay
Bernard Dyer. Otto Hehner.
Alfred C. Chapman.

King, Sidney Isaac,
49, Arundel Square, London, N.

Analytical Chemist. Student for 4 years in Chemistry and Dyeing at Bradford Technical College under Dr. Knecht and Christopher Rawson, Esq. Have also studied Chemistry and Dyeing at Herold's Institute, S.E. Am at present Technical Chemist to Messrs. Wickens Pease & Co., Ltd., Oil and Tallow Refiners, Soap Manufacturers, &c.

C. Rawson. *F. Napier Sutton.*
M. Chas. Lamb. *Samuel Rideal.*
J. Lewkowitsch. *Arthur R. Ling.*

Kewley, James,
King's College, Cambridge.

Junior Demonstrator, University Laboratory. First Class, Part I Natural Science Tripos, 1901. Major Scholar King's College B.A.

G. D. Liveing. H. J. H. Fenton.
W. H. Mills. W. J. Sell.
F. W. Dootson. H. O. Jones.
C. T. Heycock.

Landau, A. Lionel,
20, Highbury New Park, N.

Starting practice as Analytical and Consulting Chemist. Certificated Chemist of Finsbury Technical College.

Raphael Meldola — F. Southerden.
J. V. Eyre. — E. H. Miller.
Alfred C. Chapman.

Lockitt, Charles Henry, B.A. (Lond.),
5, Harley Road, S. Hampstead, London, N.W.

Assistant Master in a Secondary School. Have passed Intermediate Science Exam., Lond. Univ. (1st Division). Have for some time been working at B.Sc. Chemistry. Have taught a little chemistry in a Grammar School. Am desirous of following modern developments in the subject.

J. Herbert Allworthy. — Alexander W. Bain.
J. W. Shepherd. — Fred. Bedford.
Fredk. A. Drake.

Mathieson, Robert, J.P.,
Rillbank, Innerleithen, Peebleshire.

Chemist, Druggist, and Manufacturing Chemist. Formerly Student of Analytical and Physical Chemistry at Gordon's College, Aberdeen, and University of Edinburgh. Desire to keep informed as to the latest developments in Chemical Science, and to obtain a knowledge of the most recent analytical processes.

Stevenson Macadam. — *William Duncan.*
Adam Gibson. — *Wm. Hall Jowett.*
Robt. Carruthers. — *J. W. Clayton.*

Mence, George Augustus Henry, B.Sc., Lond.,
Ouse Villa, St. Ives, Hunts.

Teacher of Chemistry and Physics. Science Master at the Border School. Sometime a Student at the Technical College, Finsbury.

Gerald T. Moody. — William A. Davis.
Richard Berncastle. — *George Harker.*
Edward W. Lewis.

Macknight, Alexander,
Brucefield, Whitburn, N.B.

Analytical Chemist and Assayer. At present Chemist to the paper mills at Rishton and Whiteash, Lancashire. Three years as Student-Assistant to the late Dr. Macadam, Edinburgh, during which time

classes were taken at Edinburgh University. One year attending classes on Metallurgy, Assaying, &c., at the Glasgow Technical College. Since then having acted as Assistant to Dr. Aitken, Edinburgh, until present appointment was obtained. Recently elected as a member of the Edinburgh Geological Society.

Stevenson Macadam. A. Humboldt Sexton.
W. Ivison Macadam. George Smith.

G. G. Henderson.

Martindale, William Harrison,

10, New Cavendish Street, London, W.

Analytical and Pharmaceutical Chemist. Ph.D. Marburg. Holding the Major Certificate of the Pharmaceutical Society of Great Britain.

Thomas Tyrer. Otto Hehner.
Thos. Stevenson. *David Howard.*

D. Lloyd Howard.

Peck, John Wicliffe,

28, West Elba Road, Harlesden, N.W.

Pharmaceutist to the Hospital for Sick Children, Great Ormond Street, W.C., and Bacteriological Assistant to the Hospital. Pharmaceutical Chemist and Student of Analytical and Bacteriological Chemistry. I desire to be more fully in touch with the highest developments of chemical knowledge.

J. A. Dewhurst. Theophilus Pitt.
Edwd. Brooke. R. F. Wood Smith.
Reginald G. Halstead. R. L. Jenks.

Wyndham R. Dunstan.

Ramshaw, Walter,

5, Fronwen Terrace, Brecon.

Science Teacher. Teacher of Chemistry, County School, Brecon. Three years Student in Chemical Department of the Yorkshire College, Leeds.

Arthur Smithells. J. McCrae.
J. B. Cohen. Herbert Ingle.

H. D. Dakin.

Revis, Cecil,

77, King Street West, Hammersmith, W.

Chief Analyst to Messrs. Welford & Sons, Ltd., Maida Vale, W. The following papers have been published: "New Derivatives of

α-Hydrindone" (*P. Chem. Soc.*, 1895, 214); New Derivatives of α-Hydrindone" (*Trans. Chem. Soc.*, 1897, 71, 239); "α-Bromocamphor-sulpholactone" (*P. Chem. Soc.*, 1896, 247); "π-Bromocamphor, Derivatives of" (*P. Chem. Soc.*, 1896, 77). [In conjunction with Dr. F. S. Kipping.] "A Polarimetric Method of Estimating Tannin" (*Analyst*, 23, No. 263) [with Mr. R. F. Wood-Smith]; "A New Method of Examining Milk for various Bacteria" (*J. Path. Bact.*, June, 1901).

Henry E. Armstrong. Gerald T. Moody.
Alf. W. Stokes. William A. Davis.
T. Martin Lowry.

Roberts, Jonathan Hugh,
Oban Gwys, Swansea.

Science Lecturer. Graduate in Chemistry, Oxford University. Senior Science Master, Ripon School.

W. W. Fisher. J. E. Marsh.
V. H. Veley. P. Elford.
John Watts.

Scholes, William,
151, Ainsworth Road, Radcliffe, Lancs.

Science Teacher. Associate, Royal College of Science, Lond. (1st Class Chem.). First Class Honours, Pract. S. and. A. Exam., 1896. Chemistry Teacher, Ramsbottom Technical School.

William A. Tilden. G. T. Morgan.
W. Palmer Wynne. R. L. Taylor.
M. O. Forster. J. H. Wolfenden.

Taylor, Thomas,
12, Ancaster Drive, Great Western Road.

Chemical Manufacturer. I have studied at the Glasgow and West of Scotland Technical College for four years, and took the diploma in Chemistry. Appointed Lecture Assistant to Professor Henderson, 1899—1900. Lecture Assistant to Professor Purdie, St. Andrews, 1900—1901. Associate of the Institute of Chemistry.

G. G. Henderson. James Robson.
Thomas Purdie. Matthew A. Parker.
Thomas Gray.

Tindall, Arthur Lea Butler,
41, Sunnyside Rd., Ilford.

Schoolmaster. B.A. Science Honours, Camb. 1890, M.A. 1896. Teaching Chemistry.

Frank Dixon. W. H. C. Jemmet.
Stuart Blofeld. *A. Hyder.*
P. H. Grant.

Trimen, Stephen Herbert,
61, St. John's Park, London, N.

Assistant Chemist in the Customs House Branch of the Government Laboratory. I was educated at Highgate School and left there to study Chemistry under Prof. Meldola, F.R.S., at the City and Guilds Technical College, Finsbury. I was there four years, during the last of which I acted as Senior Student or Junior Demonstrator in the Chemical Dept., after gaining the Certificate of the College. I left there in 1900 to take up a temporary appointment in the Laboratory of the London County Council under Prof. F. Clowes, D.Sc. When that terminated, I obtained the post as Assistant Chemist in the Manbré Saccharine Co.'s Works at Hammersmith, and left there at the end of October, 1901, since when I have been in my present position, as above.

Raphael Meldola. Frank Clowes.
T. E. Thorpe. James Connah.
W. Williamson.

Tunnicliffe, William Wright,
Newhall, Burton-on-Trent.

Headmaster of the Central Board School, Newhall, Burton-on-Trent (No. of scholars in average attendance, 650). 1. Trained Certificated Teacher of the First Class. 2. Passed London University Intermediate Science Examination. 3. Obtained Honours in Practical and Theoretical Chemistry at the Science and Art Department's Examinations. 4. Pupil of Dr. Chas. F. Baker, late of the Birmingham University. 5. Taught Chemistry to large classes in preparation for the Examinations of the Science and Art Department for the last seven years.

William A. Tilden. C. F. Baker.
M. O. Forster. *Chapman Jones.*
G. T. Morgan. *James C. Philip.*

Wain, William Charles,
Sydney, New South Wales.

Mercantile Explosive Department. Late Chief Assistant Government Analyst, Queensland. Now Chief Chemist and Inspector of Explosives for New South Wales.

Harold Harris. Alexander Orr.
John C. H. Mingaye. *W. M. Doherty.*
B. H. Bennetts.

Wilkinson, Edward John,
8, Blenheim Terrace, Leeds.

Lecturer in Dyeing, University College of Wales, Aberystwyth.

Three years a Student in the Chemical and Dyeing Departments of the Yorkshire College. For one year Assistant in the Dyeing Department, Yorkshire College. Joint author with Mr. A. G. Perkin of *Proc. Chem. Soc.*, **16**, No. 142, 182.

J. J. Hummel.	Henry R. Procter.
Arthur Smithells.	A. G. Perkin.
Julius B. Cohen.	H. M. Dawson.
Andrew Turnbull.	Herbert Ingle.

Wood, Frank Stanley,

25, Suffolk St., Newland, Hull, Yorkshire.

Cement Works Chemist. Student Royal College of Science, 1889—1890. 1890—1894 in charge of Chemical Laboratory of the late Henry Farja, M.I.C.E. Portland Cement research work and analysis. 1894—1897 similar work for his successor, D. B. Butler, F.C.S. 1897—1902. Chief Chemist, with five subordinates, at the Cement Works of Messrs. G. and T. Earle, Limited, Hull.

D. B. Butler.	Jas. Baynes.
E. G. Clayton.	*Harold M. Ready.*
Fred. E. Johnson.	*Bertram Blount.*
George F. Holloway.	*G. Carr Robinson.*

Young, Thos. A,

318, Cheetham Hill Road, Manchester.

Manufacturing and Consulting Chemist, &c. Five years student in the laboratory of Dr. Burghardt, Manchester. Student, Owens College. Specialist in Colour Manufacture, &c. Director, 'Ircena' Colour Company.

Walter Ratcliffe.	George J. Allen.
Arthur E. Thornton.	Charles A. Fogg.

T. M. Nightingale.

The following Certificate is authorised by Council under Bye-Law I. (3).

Dobson, Henry Arthur,

"Cairne Regis," Peisley St., Orange, N.S.W.

Analytical Chemist. Late Manager, Lyndhurst Gold Fields, Ltd., Mandurama, N.S.W. Cyanide Chemist, Burdett G. M., Ltd., Near Orange, N.S.W. Studied Chemistry in the Cambridge University Chem. Lab., and also in the Auckland University Chem. Lab. (N.Z.).

Thomas H. Easterfield.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY

Issued 7/5/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. **No. 251.**

Wednesday, April 30th, 1902. Professor EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs:

Ferris, Percy J., Heathfield, Seymour Grove, Old Trafford, Manchester.
Gow, Alexander, 38, Clarendon Street, Cambridge.
Hann, Archie Cecil Osborn, 54, Wood Vale, Forest Hill, S.E.
Harrison, Walter Ernest, 43, Mostyn Road, Handsworth, Staffs.
O'Connor, Sinnott Valentine, 14, Selskar Street, Wexford.
Ralph, Stephen Jamieson, 22, Stanley Place, Eccleston Square, S.W.
Ralphs, Edwin, Hong-Kong.

A Ballot for the Election of Fellows was held, and the following were declared duly elected:—

James Samuel Ashe.
Frederic Guy S. Baker, B.A.
Cyril Bergtheil.
Richard Blenkinsop.
Ernest Boardman, B.Sc.
Alexander Bruce, B.Sc.
Fred. Carrodus.
G. H. A. Clowes, Ph.D.
Arthur James Cook.
James Codrington Crocker, B.A.
Henry Crookes.
Charles Benson Davis.
Henry Arthur Dobson.
Walter Everitt.
J. Arthur Gill.
John T. Griffiths.
Gilbert Gunn.
Arthur Hopwood.
Frank Eustace King, B.Sc.
Sidney Isaac King.
James Kewley, B.A.
A. Lionel Landau.
C. H. Lockitt, B.A.
Alexander Macknight.
William H. Martindale, Ph.D.
Robert Mathieson.
George A. H. Mence, B.Sc.
John Wicliffe Peck.
Walter Ramshaw.
Cecil Revis.
Jonathan Hugh Roberts, B.A.
William Scholes.
Thomas Taylor.
Arthur Lea B. Tindall, M.A.
Stephen Herbert Trimen.
William Wright Tunnicliffe.
William Charles Wain.
Edward John Wilkinson.
Frank Stanley Wood.
Thos. A. Young.

Of the following papers those marked * were read :—

***64. "The preparation of absolute alcohol from strong spirit." By S. Young, D.Sc., F.R.S.**

The strongest spirit that can be obtained by distillation with the most perfect still-head contains less than 96 per cent. by weight of pure alcohol. In order to remove the remainder of the water, dehydrating agents have always been employed, but they do not give very satisfactory results; according to Mendeléeff, freshly ignited lime is the only one by means of which pure dry alcohol can be prepared, and, even with this substance, special precautions have to be taken to ensure success. More recently, Squibb has obtained alcohol of still lower specific gravity by the long continued action of lime in a percolator, but his results, unlike those of Mendeléeff, were somewhat variable.

The method of dehydration recommended by the author depends on the fact that when a mixture of alcohol, benzene, and water is distilled, separation tends to take place into (1) a ternary mixture of alcohol, benzene, and water boiling constantly at 64·85°; (2) one of three possible mixtures of constant boiling point, (*a*) alcohol-benzene, b. p. 68·25°; (*b*) benzene-water, b. p. 69·25°; (*c*) alcohol-water, b. p. 78·15°; (3) one of the three pure substances, alcohol, b. p. 78·3°; benzene, b. p. 80·2°; water, b. p. 100°.

For example, when a mixture of equal weights of 93 per cent. alcohol and benzene is distilled, the fractions are (1) the ternary mixture containing, theoretically, the whole of the water; (2) the binary alcohol-benzene mixture; (3) pure alcohol.

Pure benzene and dilute alcohol are easily recovered from the ternary and binary mixtures, and there is practically no loss of material.

Theoretically, a single distillation should be sufficient to remove the whole of the water, but the separation is a difficult one, and even with a very efficient still-head a second, or even third, distillation with more benzene is necessary; the water may thus be completely eliminated, but there appears to be a trace of benzene left in the alcohol. This trace of benzene may be completely removed by distillation of the dehydrated alcohol with *n*-hexane; the binary hexane-alcohol mixture which comes over first carries the benzene with it and no hexane is left in the residual alcohol.

The observed specific gravities of dehydrated alcohol are as follows :

Mendeléeff, by means of lime	0·80625	at 0°/4°
Young, by means of benzene	0·80634	„
„ „ benzene and hexane..	0·80627	„

***65. "On the properties of mixtures of the lower alcohols with water." By S. Young, D.Sc., F.R.S., and Miss E. C. Fortey, B.Sc.**

Methyl alcohol does not form a mixture of minimum boiling point with water, and, contrary to general opinion, dry methyl alcohol can be easily obtained by distillation of the dilute alcohol with an efficient still-head. The alcohol so obtained is drier than when the strongest dehydrating agents are used.

As regards the purification of the other six alcohols investigated, distillation with benzene gave the best results with ethyl, *iso*propyl, *n*-propyl, and tertiary butyl alcohols; this treatment was also found useful in the case of *iso*butyl and *iso*amyl alcohols for the removal of lower homologues. All these alcohols were found to form mixtures of minimum boiling point with water. The boiling points and the composition of these mixtures of constant boiling point were determined, also the contraction which occurs on mixing the alcohols with water in various proportions, and the approximate temperature changes for certain mixtures. It was found that (*a*) the differences in boiling point between the alcohol and the alcohol-water mixtures of constant boiling point, (*b*) the molecular percentages of water in these mixtures, follow the same order as the boiling points of the alcohols themselves. So far as experiments have been made, the heat evolution diminishes or the heat absorption increases as the boiling points of the alcohols rise.

As regards the primary alcohols, the percentage contractions on mixing with water diminish as the boiling points of the alcohols rise, but irregularities were observed with the secondary and the tertiary alcohols investigated.

The experiments show that as the molecular weights of the alcohols increase, the attractions of their molecules for those of water diminish, but the constitution as well as the composition of the alcohols must be taken into account. The constant boiling point mixtures which the alcohols form with water are in no case hydrates of the alcohols.

***66. "On the properties of mixtures of the lower alcohols with benzene and with benzene and water." By S. Young, D.Sc., F.R.S., and Miss E. C. Fortey, B.Sc.**

Of the seven alcohols examined, all except *iso*amyl alcohol form mixtures of constant boiling point with benzene. The boiling points of these mixtures and the molecular percentages of benzene in them follow the same order as the boiling points of the pure alcohols. The boiling point of the *iso*butyl alcohol-benzene mixture is very near that of benzene itself; neither *iso*amyl alcohol nor any other alcohol with a

higher boiling point can form a mixture of constant boiling point with benzene.

Of these alcohols, only ethyl, *iso*propyl, *n*-propyl, and tertiary butyl alcohols form ternary mixtures of constant boiling point with benzene and water. When a mixture of methyl alcohol, benzene, and water is distilled, the first fraction consists of the binary alcohol-benzene mixture, and when a mixture of either *iso*butyl or *iso*amyl alcohol with benzene and water is distilled, the first fraction consists of the binary benzene-water mixture. No alcohol of this series with a boiling point higher than that of *iso*butyl alcohol can form a ternary alcohol-benzene-water mixture of minimum boiling point; with these higher alcohols, the first fraction will always consist of the binary benzene-water mixture.

The boiling points and the composition of the binary alcohol-benzene and the ternary alcohol-benzene-water mixtures have been determined.

***67. "Fractional distillation as a method of quantitative analysis." By S. Young, D.Sc., F.R.S., and Miss E. C. Fortey, B.Sc.**

It has already been pointed out (Young, *J. Soc. Chem. Ind.*, 1900, 19, 1072) that the composition of a mixture of two homologous substances can be ascertained with a fair degree of accuracy from the results of one or more fractional distillations with a very efficient still-head without bringing about anything like a complete separation of the components.

The method has now been found applicable, not only to mixtures which separate normally into their original components, whether homologous or not, but also to cases in which binary or ternary mixtures of constant boiling point are formed, such mixtures behaving, as regards distillation, like pure substances. It depends on the following facts. In the case of a mixture which tends to separate into two components, the weight of distillate that comes over below the temperature midway between the boiling points of the two components—whether single substances or mixtures of constant boiling point—is almost exactly equal to that of the more volatile component. If the original mixture tends to separate into more than two components, the weight of these components will be very nearly equal to the weight of distillate below the first middle point, the weights of distillates between the successive middle points, and the weight above the last middle point respectively.

When a binary mixture of constant boiling point is formed, the method may be employed for the determination of its composition if that of the original mixture is known, or of the original mixture if that of the binary mixture is known; when the original mixture tends to separate

into a ternary mixture, a binary mixture, and a single substance, the composition of the ternary mixture may be ascertained if that of the binary mixture and of the original mixture are known.

There are a few cases such as that of ethyl alcohol and water, or of benzene and *n*-hexane, to which the method is not applicable. In these, the curve representing the relation between boiling point and molecular composition is exceedingly flat where the more volatile component is in large excess. When this is so, the separation by fractional distillation of the more volatile component, whether a single substance or a mixture of constant boiling point, is practically impossible.

***68. "On the vapour pressures and boiling points of mixed liquids." By S. Young, D.Sc., F.R.S.**

The question as to what should be regarded as the normal behaviour, with reference to their vapour pressures and boiling points, of mixtures of two liquids soluble in each other in all proportions, has been discussed by several investigators.

It seemed probable that the simplest possible relations would be observed in the case of two such closely related substances as chlorobenzene and bromobenzene, the critical points of which are the same, whilst the ratio of the boiling points on the absolute scale is constant at all equal pressures. Other simple physical relations exist between these substances, and no perceptible heat change or volume change occurs on mixing them.

The boiling points of several mixtures of chlorobenzene and bromobenzene were determined over a range of about 100 mm., and the results are in accurate accordance with the law which Van der Waals states should hold good for two liquids the critical points of which are equal, and for which $a_{1\cdot2} = \sqrt{a_1 . a_2}$ (Galitzine, Berthelot), where $a_{1\cdot2}$ represents the mutual attraction of the unlike molecules and a_1 and a_2 the attractions of the like molecules.

The law may be stated thus: The relation between the vapour pressures and the molecular composition of mixtures of such substances is represented by a straight line: or $P = \frac{p.P_A + (100-p)P_B}{100}$, where P, P_A, and P_B are the vapour pressures of the mixture and of the two pure components, A and B, at the same temperature, and p is the molecular percentage of one of them.

***69. "The correction of the boiling points of liquids from observed to normal pressure." By S. Young, D.Sc., F.R.S.**

Crafts (*Ber.*, 1887, 20, 709) gave a convenient table for the correction of the boiling points of liquids from observed to normal pressure. There are, however, a few misprints in the table, and since then accurate determinations of the vapour pressures of a large number of pure substances have been made; it therefore seems desirable to give a revised and enlarged table for reference.

Crafts gave mean values of $\frac{\Delta t}{\Delta p}.\frac{1}{T}$ for pressures between 720 and 770 mm., but it seems more convenient, on the whole, to give the values of $\frac{dt}{dp}.\frac{1}{T}=C$ at 760 mm.

Various relations exist between the values of C and the chemical composition and constitution of the substances considered, and there is clearly a connection between the variations in the values of C and of other constants which have been considered in previous papers, such as $\frac{Dc}{D'c'}$, the ratio of the actual to the theoretical density at the critical point.

***70. "Vapour pressures and specific volumes of *iso*propyl *iso*butyrate." By S. Young, D.Sc., F.R.S., and Miss E. C. Fortey, B.Sc.**

By the electrolysis of potassium *iso*butyrate, the yield of di*iso*propyl was found to be very poor, but a fair quantity of *iso*propyl *iso*butyrate was obtained. As this ester contains two *iso*-groups, it was thought that it would be of interest to determine its vapour pressures, specific volumes, and critical constants. For the sake of comparison, a second specimen of the ester was prepared from *iso*propyl alcohol and *iso*butyric acid, and the boiling points and specific gravities of the two specimens were found to agree perfectly.

Unfortunately, *iso*propyl *iso*butyrate is much less stable than any of the ten esters previously examined (Young and Thomas, *Trans.*, 1893, 63, 1191), for some decomposition takes place at 230° and the rate of decomposition increases rapidly with rise of temperature. It was therefore impossible to make trustworthy determinations of the critical temperature or pressure, so only the vapour pressures and specific volumes at and below 230° are given.

Discussion.

Professor Thorpe said, in reference to the observations which had been made by the author concerning the properties of the hydrated alcohols and the thermal disturbance and alteration in volume accompanying the admixture of alcohols with water, that it appeared to be a tradition in the Revenue Service that on mixing ordinary (ethyl) alcohol and water, the combination, or association, of water and alcohol was only completed after a certain lapse of time, or, in other words, the mixture required to stand for some time before it acquired a constant volume, or, what comes to the same thing, a constant relative density. On what experimental evidence this belief was based was unknown to him, and direct observation made under his direction in the Government Laboratory, by Mr. John Holmes, showed that in reality the tradition had no foundation in fact. It probably had its origin in a statement in the original paper by Blagden and Gilpin that the mixtures of alcohol and water employed by them in their classical experiments, when made, were set aside for some months, in order that, as stated by them, the "interpenetration" of the parts should be complete. It seems to have been taken for granted, in fact, that interpenetration, as something apart from complete and uniform miscibility, occurred on admixture, and that this operation required a certain and considerable interval of time.

The observation on the solubility of copper sulphate in methyl alcohol had been frequently made, and he believed some reference was made to it in a paper by the late Mr. Rodger and himself (*Phil. Trans.*, 1894, 185, 530). According to Forcrand, the bluish compound has the composition $CuSO_4,2CH_3OH$.

Some years ago, he made the observation that a mixture of carbon tetrachloride and methyl alcohol could be obtained which boiled several degrees lower than the boiling point of the more volatile constituent. He had studied the relation between the boiling point and composition of the mixture, determining the composition from the vapour density of the fractions (*Trans.*, 1879, 35, 544). He would be interested to know how far the quantitative results he had obtained were in conformity with the relations indicated by Dr. Young in the case of other mixtures of miscible liquids.

Mr. Pickering said that although the existence of a constant-boiling point mixture of two substances cannot be taken as proof that these two substances are combined, yet the fact that the composition is affected to a certain extent by pressure is no proof of the contrary. Aqueous solutions of hydrochloric acid can be distilled unchanged

when the composition is approximately $HCl,8H_2O$, and Roscoe and Dittmar were held to have disproved the existence of any such hydrate by showing that the composition is affected by pressure; yet, Berthelot proved that this variability did not by any means negative the existence of a hydrate, the mixture in question being one of comparative, though not of absolute, constancy. Indeed, we could not expect the composition to be unaffected by pressure, unless the compound were perfectly stable, and there were no products of its dissociation present.

The fact, also, that water can be crystallised from a solution does not in any way disprove the existence of a hydrate in solution. The water may be present only as one of the dissociation products of the hydrate, and whether it or the hydrate separates out depends on the circumstances of the crystallisation. Numerous instances in point might be given: thus, water may be crystallised from a 20 per cent. solution of sodium hydroxide, though such a solution will, under other conditions, yield crystals of the heptahydrate, of which it is chiefly composed.

Dr. DIVERS mentioned, in connection with the author's account of the solution of anhydrous copper sulphate, with blue colour, in anhydrous methyl alcohol, that W. Wislicenus and Stoeber had recently pointed out (*Ber.*, 1902, 35, 540) that anhydrous cupric acetate dissolves in methyl alcohol when boiled with it, giving a deep green solution which deposits crystalline cupric methoxide-acetate, $CH_3OCuC_2H_3O_2$, if the boiling be prolonged.

Professor YOUNG replied that they had not yet investigated the mixture of carbon tetrachloride and methyl alcohol, but agreed that it would be interesting to determine the composition of the mixture of minimum boiling point by the distillation method, in order to compare the result with that obtained by Professor Thorpe from the vapour density.

He did not regard the variability of the composition of the mixtures of minimum boiling point with the pressure as a sufficient proof, but only as strong confirmatory evidence as to the non-existence of hydrates of the alcohols. The reasons for believing that such hydrates do not exist are fairly numerous, whilst the only ground for assuming that the liquids under consideration are hydrates seems to be that they boil at a constant temperature. Yet the very fact that the boiling points are lower than those of the alcohols themselves or than that of water indicates that the attraction of the unlike molecules is small compared with the attractions of the like molecules, and this could hardly be the case if hydrates were formed. With regard to the interesting action of anhydrous copper acetate on methyl alcohol, he might mention that Beilstein describes a crystalline alcoholate of copper sulphate, $CuSO_4,CH_3OH$.

***71. "The preparation of highly substituted nitroaminobenzenes." By K. J. P. Orton.**

The methods at present known of preparing nitroaminobenzenes from anilines are scarcely applicable when the anilines possess two ortho-substituents. The following procedure has been devised, and in most cases gives a quantitative conversion of the aniline into the nitroamine.

To a solution of the aniline (1 part) in glacial acetic acid (25 parts) is added nitric acid (sp. gr. 1·5; 0·75 to 1 part); acetic anhydride (0·75 to 1 part) is slowly added to the cooled mixture. Heat is developed, and the aniline nitrate dissolves, forming a solution of the nitroamine.

By this means, the following nitroamines have been prepared:

1-Nitroamino-3-tribromobenzene and 1-nitroamino-*s*-trichlorobenzene (this vol., p. 58); *1-nitroamino-2:6-dichloro-4-bromobenzene*, and *1-nitroamino-2:4-dichloro-6-bromobenzene*, $C_6H_2Cl_2Br\cdot NHNO_2$, *1-nitroamino-2-chloro-4:6-dibromobenzene*, and *1-nitroamino-4-chloro-2:6-dibromobenzene*, $C_6H_2ClBr_2\cdot NHNO_2$; these four substances crystallise in needles (from water), and all melt and decompose at 136—138°; their *barium* salts crystallise in plates with $1H_2O$. The *N-methyl ether* of nitroamino-*s*-tribromobenzene, $C_6H_2Br_3\cdot NMeNO_2$, obtained from the sodium salt and methyl iodide, forms four-sided prisms melting at 95·5°.

1-Nitroamino-2:4-dibromo-6-nitrobenzene, $NO_2\cdot C_6H_2Br_2\cdot NHNO_2$, m. p. 91—92°, forms yellow plates (from water); *1-nitroamino-2:3:4:6-tetrabromobenzene*, plates melting and decomposing at 136°; *1-nitroamino-2:4:6-tribromo-3-nitrobenzene*, yellow, four-sided prisms, melting and decomposing at 108—109°; *1-nitroamino-2:4-dichlorobenzene*, lustrous leaflets from petroleum, melting at 55—56°. The *barium* salt of the last-mentioned substance crystallises in plates with $3\frac{1}{2}H_2O$.

4-Nitroamino-3:5-dibromotoluene, $CH_3\cdot C_6H_2Br_2\cdot NHNO_2$, forms slender needles melting and decomposing at 122—123°; *2-nitroamino-3:5-dibromotoluene*, needles, melting at 112° and decomposing at 122°; the *barium* salts from each substance crystallise with $1H_2O$.

When nitroamino-*s*-trisubstituted benzenes contain a bromine atom in the para-position relative to the $\cdot NHNO_2$ group, the nitro-group is capable of displacing the *p*-bromine atom, giving a di-*o*-substituted *p*-nitroaniline. The majority of these nitroamines dissolve in concentrated sulphuric acid, forming a deep purple or violet solution; in the case of nitroamino-2:4-dichlorobenzene, which has an *o*-hydrogen atom, addition of water immediately destroys the purple colour, and a yellow

precipitate of 2 : 4-dichloro-6-nitroaniline is formed; in the case of the other nitroamines, in which the hydrogen atoms in positions 2, 4, and 6 are replaced by other atoms or groups, water precipitates from the purple solution a red solid; the latter contains among other substances a di-*o*-substituted *p*-nitroaniline if the original nitroamine had a *p*-bromine atom. The purple solutions in sulphuric acid may possibly correspond to an intermediate stage between the nitroamine and the nitrated aniline.

***72. "The atomic weight of tellurium. Preliminary notice."**
By A. Scott.

The many attempts to determine the atomic weight of tellurium which have been published since Mendeléeff published his well-known table of elements indicate very clearly the general recognition that experimental results did not sanction the assignment of a lower atomic weight to tellurium than that of iodine. The problem was rendered more complicated by the variations in the numbers obtained by the same experimenter when he employed different methods in his determinations. This gave rise to the suspicion that the substance purified by the best methods was, or at least might be, a mixture of the true tellurium with a higher homologue. All the most recent researches, and especially those of Pellini (*Ber.*, 1901, **34**, 3807) and of Köthner (*Annalen*, 1901, **319**, 1), seem conclusively to prove, however, that the atomic weight of tellurium is very near 127·64, that of iodine being 126·85. For more than a year the author has been at work on this subject and his results are entirely in agreement with those of the above-mentioned experimenters. It was obvious that the most satisfactory substance for such determinations should contain both tellurium and iodine and be weighted with as little as possible of other elements. Such a substance is trimethyl tellurium iodide, which is easily prepared and purified, is very stable, and non-hygroscopic. When tellurium is heated to 80—100° in a sealed tube with methyl iodide (Demarçay, *Bull. Soc. Chim.*, 1883, **40**, 100), dimethyl tellurium di-iodide is readily formed; when this is treated with reducing agents in presence of methyl iodide, trimethyl tellurium iodide, $Te(CH_3)_3I$, is readily obtained. The corresponding bromide is a salt very well adapted for titration with silver by the method of Stas. Preliminary determinations so far agree with all the best results hitherto published in proving that the atomic weight of tellurium is nearly a unit higher than that of iodine.

In the following determinations, all the weights given are corrected for errors in face values of the weights, as well as being brought to vacuum standards:

$Te(CH_3)_2I$.	AgI.	
1·7461 gave	1·3688	∴ $Te(CH_3)_2I = 299·62$ and $Te = 127·70$.
6·6425 „	5·20575	∴ $Te(CH_3)_2I = 299·58$ „ $Te = 127·66$.
8·0628 „	6·3181	∴ $Te(CH_3)_2I = 299·61$ „ $Te = 127·69$.

By titration:

$Te(CH_3)_2Br$.	Ag.	
2·4294 required	1·0373	∴ $Te(CH_3)_2Br = 252·79$ and $Te = 127·77$.
6·8424 „	2·9201	∴ $Te(CH_3)_2Br = 252·90$ „ $Te = 127·88$.

The second sample of bromide was not so pure as the first, as it was the second crop of crystals obtained from the mother liquors. The mean value is therefore Te = 127·74 taking all five determinations, or 127·70 if only the first four be taken.

Pellini gives 127·64.
Köthner „ 127·63.

The author indicated by a graphic representation of the quotients, $\frac{F}{O} = 1·190$, $\frac{Cl}{S} = 1·105$, $\frac{Br}{Se} = 1·009$, $\frac{I}{Te} = 0·993$, obtained by dividing the atomic weights of the halogen elements by those of the corresponding members of the oxygen group respectively, why he thought it very unlikely that the atomic weight of iodine should exceed that of tellurium.

In making the necessary calculations, the following values were taken: C = 12·00; H = 1·0075; I = 126·85; Br = 79·95 (O = 16).

Two syntheses of silver iodide were made, as follows:

Ag.	AgI.	
4·6240 gave	10·0634	∴ AgI = 234·89 and I = 126·96.
6·39978 „	13·92913	∴ AgI = 234·91 „ I = 126·98.

Substituting I = 126·97 for I = 126·85 in the first three calculations increases the values for $Te(CH_3)_2I$ by 0·15, and those for Te by 0·03.

73. "Nitrogen bromides containing the propionyl group."

By F. D. Chattaway.

Propionanilide and the bromopropionanilides readily react with hypobromous acid, the imino-hydrogen being replaced by bromine, a hypobromite being probably formed as an intermediate product.

The action is a reversible one, and when nitrogen bromides are placed in water the opposite change takes place until a position of equilibrium is reached.

Except in colour, these nitrogen bromides closely resemble the corresponding nitrogen chlorides. All show the characteristic behaviour

of the nitrogen halogen linkage, and readily react with hydriodic acid, sulphurous acid, hydrogen sulphide, alcohol, and potassium cyanide.

When an unsubstituted or partially substituted phenyl residue is attached to the nitrogen, they very readily undergo isomeric change. Interchange between bromine attached to the nitrogen and hydrogen in the ortho-position in an unsubstituted nucleus has not been observed. Apparently the halogen cannot pass from the nitrogen to a meta-position.

All nitrogen bromides, when treated with an excess of hydrobromic acid, are decomposed, bromine being liberated and the corresponding anilide re-formed. On the other hand, when an anilide is treated with an excess of bromine, a nitrogen bromide and hydrobromic acid are produced.

A large excess of hydrobromic acid or the continuous removal of the free bromine causes the anilide to be re-formed, whilst the addition of a salt of a weaker acid which can remove the hydrobromic acid causes the action to proceed in the opposite direction and a nitrogen bromide is produced. The reversible nature of this reaction is most clearly seen when the nucleus is already fully substituted, as otherwise isomeric change and substitution into the ring may take place.

The following substances have been prepared:

Propionylphenyl nitrogen bromide, $C_6H_5 \cdot NBr \cdot CO \cdot C_2H_5$, pale yellow pyramids, m. p. 88°; p-*bromopropionanilide*, $C_6H_4Br \cdot NH \cdot CO \cdot C_2H_5$, rectangular plates, m. p. 149°; *propionyl*-p-*bromophenyl nitrogen bromide*, $C_6H_4Br \cdot NBr \cdot CO \cdot C_2H_5$, yellow prisms, m. p. 78°; *propionyl*-p-*bromophenyl nitrogen chloride*, $C_6H_4Br \cdot NCl \cdot CO \cdot C_2H_5$, colourless plates, m. p. 59°; o-*bromopropionanilide*, $C_6H_4Br \cdot NH \cdot CO \cdot C_2H_5$, colourless prisms, m. p. 93°; *propionyl*-o-*bromophenyl nitrogen bromide*, $C_6H_4Br \cdot NBr \cdot CO \cdot C_2H_5$, yellow prisms, m. p. 117°; *propionyl*-o-*bromophenyl nitrogen chloride*, $C_6H_4Br \cdot NCl \cdot CO \cdot C_2H_5$, colourless rhombs, m. p. 59°; 2:4-*dibromopropionanilide*, $C_6H_3Br_2 \cdot NH \cdot CO \cdot C_2H_5$, colourless needles, m. p. 136°; *propionyl* 2:4-*dibromophenyl nitrogen bromide*, $C_6H_3Br_2 \cdot NBr \cdot CO \cdot C_2H_5$, yellow rhombs, m. p. 87°; *propionyl* 2:4-*dibromophenyl nitrogen chloride*, $C_6H_3Br_2 \cdot NCl \cdot CO \cdot C_2H_5$, colourless plates, m. p. 71°; 2:4:6-*tribromopropionanilide*, $C_6H_2Br_3 \cdot NH \cdot CO \cdot C_2H_5$, colourless prisms, m. p. 203°; *propionyl* 2:4:6-*tribromophenyl nitrogen bromide*, $C_6H_2Br_3 \cdot NBr \cdot CO \cdot C_2H_5$, yellow prisms, m. p. 82°; *propionyl* 2:4:6-*tribromophenyl nitrogen chloride*, $C_6H_2Br_3 \cdot NCl \cdot CO \cdot C_2H_5$, colourless prisms, m. p. 75°.

The next meeting will be held on **Thursday, May 15th, at 8 p.m.**

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 23/5/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. No. 252.

Thursday, May 15th, 1902. Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs:

James Handby Ball, St. Stephen's Villa, Limerick.
Bryce Chudleigh Burt, University Settlement, Bermondsey, S.E.
Arthur Crozier Claudet, 27, Daleham Gardens, Hampstead, N.W.
Edgar William Foll, 40, Sutton Street, Lambeth, S.E.
John Longsdon Garle, 136, Holland Road, Kensington, W.
George H. Leader, Sexey's School, Blackford, Somerset.
James Butler Moody, 111, Manchester Road, Burnley, Lancs.
Percy Philip Phillips, Haslemere, Morris Avenue, Manor Park, E.
William E. F. Powney, 67, Barretts Grove, Stoke Newington, N.
William C. S. Stanger, 72, Belle Vue Road, Ipswich.

Of the following papers, those marked * were read:

***74. "The variation with temperature of the surface-tensions and densities of liquid oxygen, nitrogen, argon, and carbon monoxide." By E. C. C. Baly and F. G. Donnan.**

The measurements were made by the method of elevation in capillary tubes. The surface-tensions, molecular surface-energies, and densities of liquid oxygen, nitrogen, argon, and carbon monoxide have been determined between the temperatures of 70° and 90° (absolute). In

the case of argon, owing to the proximity of its freezing and boiling points, measurements could only be made between 84° and 89°.

The relation between molecular surface-energy and temperature is found to be linear, thus agreeing with the results obtained by Eötvös and by Ramsay and Shields for non-associated liquids.

The values found for $\frac{d}{dt}\gamma(Mv)^{\frac{2}{3}}$, the temperature-coefficient of the molecular surface-energy, are as follows :

Oxygen.....	1·917
Nitrogen	2·002
Argon	2·020
Carbon monoxide	1·996

The average value obtained by Ramsay and Shields for non-associating liquids was 2·212.

Continuations of the straight lines connecting molecular surface-energy and temperature so as to cut the temperature-axis give values for the temperature which in the case of oxygen and nitrogen agree very closely with the critical temperatures as determined by Olszewski. In the case of argon and carbon monoxide, the temperatures so found do not agree with the critical temperatures as previously determined.

***75. "Comparison of bromonitrocamphane with bromonitrocamphor." By M. O. Forster.**

The close relationship between 1 : 1-bromonitrocamphane, $C_8H_{14}\begin{matrix}CH_2\\|\\CBrNO_2\end{matrix}$, and *aa*-bromonitrocamphor, $C_8H_{14}\begin{matrix}CBrNO_2\\|\\CO\end{matrix}$, led to the expectation that the series of changes by which the former substance is converted into a hydroxylic isomeride of camphor might be applied to bromonitrocamphor, and thus give rise to a hydroxylic isomeride of camphorquinone. Bromonitrocamphor was therefore heated with alcoholic silver nitrate until silver bromide was no longer precipitated. This treatment, which transforms bromonitrocamphane into nitrocamphene, $C_{10}H_{15}\cdot NO_2$, proceeds very slowly in the case of the camphor derivative, the solution becoming yellow. Instead of the expected nitro-compound, $C_{10}H_{13}O\cdot NO_2$, the only crystalline product obtained was camphorquinone. The yield of quinone by the new method amounted to 25 per cent.; the process, therefore, compares favourably with that of Claisen, but is more tedious.

The comparison of bromonitrocamphane with bromonitrocamphor has been extended to the behaviour of these substances towards phenylhydrazine. The uncontrolled action of the base is exceedingly vigorous and yields no definite product; under regulated conditions, however,

bromonitrocamphane is reduced to nitrocamphane, which may be thus obtained in a purer form than has been possible hitherto. Nitrocamphane prepared by this method melts at 157° instead of 147—148°, and has $[\alpha]_D = +27{\cdot}0°$ in benzene, and $+7{\cdot}4°$ in absolute alcohol, instead of 20·4° and 4·6° respectively.

In the case of bromonitrocamphor, phenylhydrazine gives rise to nitrocamphor in a form which requires to be crystallised only once from petroleum to produce the substance in the colourless state, melting at 103° and giving $[\alpha]_D = -123{\cdot}8°$ in benzene; as the yield amounts to 84 per cent. of the theoretical, this method appears to be a distinct improvement on the existing process.

Bromine has no action on bromonitrocamphor under conditions which lead, in the case of bromonitrocamphane, to elimination of the nitro-group and production of a tribromo-derivative. Bromonitrocamphor is also indifferent towards nitric acid, which transforms bromonitrocamphane into a new lactone; alkalis eliminate hydrogen bromide from this compound, yielding salts of an unsaturated acid containing nitrogen. These derivatives are being investigated.

***76. "*aa*-Benzoylnitrocamphor and *aa*-benzoyliodocamphor." By M. O. Forster and E. A. Jenkinson.**

aa-Benzoylnitrocamphor, $C_8H_{14}\begin{cases}C(NO_2)CO\cdot C_6H_5\\ CO\end{cases}$, prepared by heating 5 grams of enolic benzoylcamphor dissolved in 25 c.c. of glacial acetic acid with 1·5 c.c. of fuming nitric acid, is also produced when nitrogen peroxide is passed into a solution of benzoylcamphor in dried chloroform. It requires 40 parts of boiling alcohol to dissolve it and is sparingly soluble in common solvents, crystallising in rectangular plates which melt and evolve gas at 225°. A 2 per cent. solution in chloroform has $[\alpha]_D = +245{\cdot}2°$. It is insoluble in aqueous alkalis, is indifferent towards ferric chloride, and does not give Liebermann's reaction.

Attempts to convert the substance into *aa*-benzoylaminocamphor and *aa*-benzoylhydroxylaminocamphor have been unsuccessful, but it is readily hydrolysed by alcoholic potash, yielding α-nitrocamphor and benzoic acid.

aa-Nitrobenzoylnitrocamphor, $C_8H_{14}\begin{cases}C(NO_2)CO\cdot C_6H_4\cdot NO_2\\ CO\end{cases}$, produced when benzoylnitrocamphor is dissolved in fuming nitric acid, is more readily soluble than the foregoing substance, and crystallises from alcohol in pale yellow leaflets which melt and evolve gas at 176—177°; a 2 per cent. solution in chloroform has $[\alpha]_D = +190{\cdot}6°$.

Hydrolysis with alcoholic potash resolves the substance into nitrocamphor and *m*-nitrobenzoic acid.

aa-Benzoyliodocamphor, $C_8H_{14}<\begin{matrix}CI\cdot CO\cdot C_6H_5\\ CO\end{matrix}$, is not obtainable by the methods which give rise to the benzoylbromocamphors and benzoylchlorocamphors; it is prepared by adding a solution of iodine in potassium iodide to enolic benzoylcamphor dissolved in aqueous potash. The compound crystallises from alcohol in pale yellow plates which become reddish-brown when exposed to light; it melts at 136°. A 2 per cent. solution in chloroform has $[\alpha]_D = +47{\cdot}7°$.

Benzoyliodocamphor is not converted into an isomeride by the action of hydrobromic acid, and hydriodic acid merely reduces it. Solutions in organic liquids rapidly undergo decomposition with liberation of iodine; ferric chloride soon produces a pale green colour, becoming bluish, and finally purple. Attempts to convert the substance into benzoylcyanocamphor and benzoylhydroxycamphor have been unsuccessful.

***77. "2 : 4-Dibromo-5-nitro- and 2 : 4-dibromo-3 : 5-dinitro-toluenes and their behaviour on reduction." By W. A. Davis.**

On nitration with fuming nitric acid, 2 : 4-dibromotoluene gives 2 : 4-dibromo-5-nitrotoluene, which is converted by reduction with tin and hydrochloric acid into 4 : 6-dibromo-*m*-toluidine, the *acetyl* derivative of which crystallises from alcohol in small, white prisms (m. p. 167°.)

If the nitration of 2 : 4-dibromotoluene be not carefully regulated, 2 : 4-*dibromo*-3 : 5-*dinitrotoluene* is obtained. It crystallises from ethyl acetate in yellow prisms (m. p. 127·5°) and differs from all the other bromo- and dibromo-nitrotoluenes, as it loses the whole of its bromine on reduction with tin and hydrochloric acid, giving *s*-tolylenediamine; the *diacetyl* derivative, $C_6H_2Me(NHAc)_2$, crystallises from alcohol in small, hemimorphic prisms (m. p. 236—237°) and is strongly electric. The removal of the bromine atoms from 2 : 4-dibromo-3 : 5-dinitrotoluene during reduction is apparently due to the influence of the two contiguous nitro-groups.

***78. "Note on the purification of hydrochloric acid from arsenic." By L. T. Thorne, Ph.D., and E. H. Jeffers.**

In the estimation of arsenic by the Marsh-Berzelius test, the use of hydrochloric acid is admittedly preferable to that of sulphuric acid. It is, however, practically impossible to purchase hydrochloric acid really

free from arsenic, and it is therefore necessary to remove the last traces of arsenic from it in the laboratory.

The method recommended in the report of the Joint Committee of the Society of Chemical Industry and of Public Analysts (*Analyst*, 1902, 27, 48), namely, that of treatment of the diluted acid with hydrobromic acid or bromine and sulphurous acid and subsequent distillation is successful in most cases but occasionally fails, the arsenic then appearing to be present in a very stable or resistant form. Under these latter conditions, satisfactory results are said to be obtained if the hydrobromic and sulphurous acids are added to the *strong* hydrochloric acid and the excess of hydrochloric acid gas boiled off before distillation commences. If large quantities of hydrochloric acid are wanted, this method is inconvenient and wasteful, owing to the large quantities of hydrochloric acid gas evolved.

The whole of the arsenic may readily be removed by means of a modification of the well-known Reinsch test for arsenic in the following manner.

The hydrochloric acid to be purified is diluted with water till its specific gravity is about 1·10, then raised to the boiling point, and a piece of fine copper gauze introduced. The gauze should be of about 100 meshes to the inch, and of as pure copper as possible. When a couple of litres of liquid are being dealt with, the gauze should be about four inches square and coiled very loosely (about $1\frac{1}{2}$ to 2 turns) round a long glass rod flattened at the end, as in this way it can be readily introduced and removed, besides being brought into better contact with the liquid. The whole is then kept just boiling for an hour. By this time, the gauze will have become more or less blackened, and should be replaced by a second piece and the digestion continued for another hour. If this piece is also blackened, a third is used, and so on, until the gauze remains perfectly bright after about an hour's digestion. With moderately good acid, two, or at most three, pieces of gauze are sufficient. The gauze is then removed, and the acid at once transferred to a retort and distilled from a fresh piece of gauze. It is advisable, as a precaution, to reject the first 20 per cent. of the distillate, though even this is very rarely contaminated if the digestion is carefully carried out, and from 100 to 200 c.c. should be left behind in the retort. The method is simple and requires but little attention, and it is not necessary to use the purest acid; even good muriatic acid, "commercially free from arsenic," may be satisfactorily employed. The acid obtained is the constant boiling point acid, which is about the most suitable strength for use in the Marsh-Berzelius test.

The gauze must, of course, be gently ignited before being used, and should not be introduced until the acid is just beginning to boil. It is also preferable not to allow the digested liquid to cool in contact with

the air before transferring it to the retort, as the copper gauze would be much attacked and its efficiency for the present purpose considerably lessened by the consequent oxidation.

79. "The radioactivity of thorium compounds. Part II. The cause and nature of radioactivity." By E. Rutherford and F. Soddy.

The authors find that thorium from which ThX has been separated regains its activity with time, whilst the activity of ThX decreases with time. At the end of three weeks, the activity of the former again reached a maximum value, and the activity of the latter almost completely disappeared.

ThX possesses a distinct chemical behaviour which differentiates it from thorium. Ammonia is the only reagent of those tried capable of separating it from the latter. Ammonium carbonate, oxalic acid, and sodium phosphate give precipitates with normal activity, and the residues from the filtrates are inactive.

Using the radioactivity of the residues from the filtrates after precipitation of the thorium by ammonia, as a means of determining the amounts of ThX present, it was found that the amounts produced in varying intervals of time between successive precipitations agree with the requirement that ThX is being continuously produced by thorium compounds at a constant rate.

The rate of production of ThX and the rate of decay of its activity are apparently unaffected by known agencies. Both changes proceed independently of the chemical and physical conditions of the molecule.

The source of the energy required to maintain the radioactivity of thorium over indefinite periods is therefore to be found in a chemical change producing new types of matter.

Many of the results obtained by the authors in their investigation of the thorium emanation are now capable of explanation. Emanating power appears as a property of ThX and not of thorium, and is proportional to the activity of the ThX present. The decay and recovery of emanating power of ThX and thorium are completely analogous to the decay and recovery of radioactivity. These results find their simplest explanation in the view that a secondary change is proceeding in ThX. One of the products is gaseous, and in the radioactive state constitutes the emanation. This change appears more allied to ordinary chemical reaction than the primary, for it is affected by the conditions.

The residual activity of thorium would be explained if the chemical change which produces ThX produces also a second kind of active matter, closely allied to thorium in its properties. The radiations of this residual part are composed entirely of rays non-deviable in the magnetic field, whereas the other two components of thorium radio-

activity comprise both deviable and non-deviable radiation. In this respect, uranium and thorium are analogous (compare following paper).

The present result, that radioactivity is the consequence of changes —independent of the conditions—in which new types of matter are formed, leads to the conclusion that radioactivity is the manifestation of sub-atomic chemical change.

80. "The radioactivity of uranium." By F. Soddy.

During an investigation of the radioactivity of uranium (conjointly with Prof. Rutherford), great differences arose between the results obtained and those of previous workers. These are traced to the methods employed for measuring radioactivity.

UrX, prepared by Crookes' original method (*Proc. Roy. Soc.*, 1900, **66**, 409), although intensely active to the photographic plate, is almost inactive to the electrometer under ordinary circumstances. The uranium from which it is separated is inactive to the sensitive film, but its activity to the electrometer is very nearly normal.

This is due to the dual character of uranium radiation (Rutherford, *Phil. Mag.*, 1899, [v], **47**, 109). The α- or easily absorbed radiation is without appreciable action on the photographic film, and contributes by far the major portion of the ionisation effect observed by the electrometer. The β- or penetrating radiation, on the other hand, causes the whole of the photographic effect, but being little absorbed by gases, and constituting but a small proportion of the total radiation, its ionisation effect cannot be well observed by the electrometer without special arrangements.

UrX possesses all the β- with none of the α-radiation, the latter being completely retained by the uranium. The β- is wholly deviable in the magnetic field, the α-radiation not at all. This explains the conclusion of Becquerel (*Compt. rend.*, 1902, **134**, 208), who worked solely with the photographic method, that the whole of the uranium radiation is deviable in the magnetic field.

The discovery of Becquerel that inactive uranium recovers its activity with time (*Compt. rend.*, 1901, **133**, 977) therefore points to a continuous production of UrX by the uranium. This continuous production can be observed by means of the β-radiation in uranium originally freed from UrX after three days.

The published methods of Crookes (*loc. cit.*) and Becquerel (*Compt. rend.*, 1900, **131**, 137) fail to remove the α-radiation of uranium, or even to diminish its quantity. As in the case of thorium, this constitutes a residual activity comprising only non-deviable radiation, and it has not

yet been found possible to remove it by chemical means. Experiment shows that if it is a secondary radiation caused by UrX, it must take over a year to decay to half its value after the exciting cause is removed. It seems therefore more probable that it is caused by a second type of non-uranium matter, produced from the uranium by the same change as he UrX.

ADDITIONS TO THE LIBRARY.

I. *By Donation.*

Paetzold, Ernest. Beiträge zur pharmacognostischen und chemischen Kenntnis des Harzes und Holzes von Guajacum officinale L., sowie des "Palo balsamo." Pp. 117. Strassburg i. E. 1901. From Ed. Schaer.

Ingle, Herbert. Manual of agricultural chemistry. Pp. 412. London 1902. From the Author.

Böttger, Wilhelm. Grundriss der qualitativen Analyse vom standpunkte der Lehre von den Ionen. Pp. 249. Leipzig 1902. From the Author.

II. *By Purchase.*

Windisch, Wilhelm. Das chemische Laboratorium des Brauers. Anleitung zur chemisch-technischen Betriebskontrolle für Studierende und Praktiker. Pp. 373. Berlin 1902.

Long, John H. A text-book of urine analysis for students and practitioners of medicine. Pp. 249. Chicago 1900.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before June 9th.

At the next meeting, on **Wednesday, May 28th, at 5.30. p.m.**, the following papers will be communicated :—

"Taxin." By T. E. Thorpe, C.B., F.R.S., and G. Stubbs.

"Some excessively saline Indian well waters." By J. W. Leather.

"Soil samples." By J. W. Leather.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 12/6/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. No. 253.

Wednesday, May 28th, 1902. Professor MELDOLA, F.R.S., Vice-President, in the Chair.

Messrs. J. W. Peck, J. C. Crocker, and J. Kewley were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Edwin T. H. Bucknell, Ebley House, Parsonage St., Dursley, Glos.
Francis E. Francis, 8, Manilla Rd., Clifton, Bristol.
George Paton Pollitt, Ph.D., St. Silas Rd., Blackburn, Lancs.
Harold James Roast, 3, Manor Park Rd., Harlesden, N.W.
Edward J. Wheeler, Albany, State of New York, U.S.A.

Of the following papers, those marked * were read:

***81. "Taxine, the alkaloid of yew." By T. E. Thorpe, C.B., F.R.S., and G. Stubbs.**

The investigation has been carried out on autumn-gathered leaves of male and female trees of the species *Taxus Baccata*. The alkaloid was

extracted by digesting the powdered, air-dried leaves with 1 per cent. sulphuric acid for 5 or 6 days. The acid liquid was strained and pressed from the leaves, and at once, without concentration, rendered alkaline and extracted with ether. Taxine was obtained in the form of very fine, glistening particles by crushing down the residue from the ether extract. It gives precipitates with most of the alkaloidal reagents, and colour reactions with strong sulphuric acid alone, and when this reagent is mixed with nitric acid, molybdic acid, or chromic acid.

Taxine is very susceptible to change. At least two substances result from the action of dilute acids upon it, but owing to lack of material the authors have not yet completed their investigation of these products.

Several salts have been prepared and analysed. Two compounds with gold chloride have been obtained which have the formulæ $C_{37}H_{52}NO_{10},HAuCl_4$ (m. p. 72·5°) and $C_{37}H_{52}NO_{10},AuCl_3$ (m. p. 132—134°) respectively. The methyl iodide compound, $C_{37}H_{52}NO_{10},CH_3I$ (m. p. 121°), has been prepared as a white, amorphous powder by mixing benzene solutions of the alkaloid and methyl iodide.

Although the analytical figures deduced, both for taxine and its salts, are in substantial agreement with the formula, $C_{37}H_{52}NO_{10}$, given by Hilger and Brande (*Ber.*, 1890, **23**, 464), the authors are not of opinion that this formula is definitely established.

The alcoholic extract of yew, amounting to about 26 per cent. of the dry leaves, is at present under examination.

Discussion.

Prof. Dunstan remarked that the authors had confirmed the accuracy of previous work on the properties of taxine, and he hoped that they would now be able to go further and throw some light on its chemical structure. It had not been yet fully proved that yew-poisoning was due to the presence of taxine, and indeed even the exact conditions under which yew becomes poisonous did not appear to have been determined with certainty.

Mr. Golding said that in the year 1893 he had assisted Mr. Dymond in an investigation of the alkaloid of the yew. They found that drying the leaves at 100° destroyed the alkaloid.

The extraction of the alkaloid was made from bruised, green, freshly-gathered leaves by Marmé's process, which was repeated several times to purify the alkaloid. Further purification was effected by adding light petroleum to the ether solution, the fractions thus obtained giving the characteristic reactions of taxine.

When dry hydrogen chloride was passed into a solution of the alkaloid in anhydrous ether, and a crystalline precipitate was formed,

which soon changed to a dark brown paste, phenomena also observed by Hilger and Brande.

Cases were on record of animals eating yew with impunity, and a large number of the cases which had proved fatal were due to the eating of *withered* branches.

Dr. VOELCKER pointed out that the uncertainty with regard to poisoning by yew extended to the kind of animal eating it as well as the condition of the leaves. A good deal also depended on the conditions under which it was eaten, whether, for example, much grass or other food was eaten along with it. He thought that it was very desirable that the other substances which the authors had obtained should also be studied, but regarded it as essential that the yew examined should be freshly gathered, and not kept for some considerable time as in the case of that employed by the authors.

Mr. STUBBS, in reply, said that no work had been done to ascertain if the alkaloid contained methyl groups. He did not think that the substance had been produced by the action of the acid used for extraction upon a glucoside. The material employed had been dried in air, at a temperature not exceeding 60°. They had obtained the same amounts of alkaloid from the leaves both when freshly gathered and after they had been dried.

*82. "The sampling of soils." By J. W. Leather.

Experiments were made in India to determine the accuracy of the auger method of sampling soils, and the agreement between the samples was tested by determinations of the total nitrogen, the available phosphoric acid, and the available potash. The results showed that in most cases the agreement was very good between samples, but that in some cases the divergence exceeded 1 in 20, an amount which the author considered too great.

The amounts of phosphoric acid in some of the Rothamsted wheat soils, as found by Dyer, were considered with a view to determine the accuracy of the method of sampling which was there employed. The author considered that such a comparison indicated the Rothamsted method to have yielded as good results as the auger method. Both, however, fall short of what is expected in taking samples of commercial products, and it was urged that the newer methods of soil investigation demand more accurate methods of sampling.

DISCUSSION.

Dr. DYER said that it seemed obvious that a sample drawn from many parts of the field was more likely to be accurately representative

than a sample drawn from one or few places. Nevertheless, it seemed to him that Dr. Leather's analytical results, obtained on samples drawn from different parts of the same field, instead of indicating differences in the samples, appeared really to indicate that both the sampling and the analytical work were excellently performed. Some of the analytical figures regarded by Dr. Leather as discrepant, he (the speaker) should himself regard as being in very good agreement. As to the results of his determinations of phosphoric acid in the Rothamsted wheat soils, which Dr. Leather had quoted, it must be remembered that, whilst the samples analysed represented only the first nine inches of soil, the phosphoric acid removed in the crops might, in the case of wheat, on many plots, be drawn to a considerable extent from the subsoil; and that the influences of vegetation might considerably affect the distribution of soil constituents in the various layers of the soil and subsoil. The "original" phosphoric acid of Broadbalk field, as calculated back from the present contents and known additions and removals, showed, on the whole, as Dr. Leather had pointed out, a fair uniformity, though there were some discrepancies. It was, however, quite probable that the percentage of phosphoric acid in the surface soil was originally by no means uniform on the different plots. Certain of the plots had long behaved somewhat anomalously, indicating some inherent physical or chemical differences in the soil or subsoil.

Dr. VOELCKER was inclined to agree with Dr. Dyer, and to regard the results which Dr. Leather had obtained as being very satisfactory, and as agreeing well with one another. It would hardly be a matter for surprise to those who had followed the work at Rothamsted, and who knew the infinite pains which the late Sir Henry Gilbert always took to ensure accuracy in every detail, to learn that Dr. Leather's estimate of gains and loses showed that there could not be much amiss with the Rothamsted method of soil-sampling. Still, it was obvious that the more places in which borings of a soil were taken for sampling purposes the more representative would that sample be.

There was considerable difference between soil samples taken as at Rothamsted (where at least three holes were selected on each plot), and the block of soil ordinarily sent by a farmer when he wished his soil analysed. In the latter case, no doubt, the method Dr. Leather suggested would give a much more representative sample.

The difficulty was in the case of soils of stony character, or where lumps of chalk occurred. The auger might very readily, by pushing these stones or lumps aside, or by including them in the boring, ultimately cause a considerable difference in the analysis.

Mr. HALL said that for some years he had been using an auger for taking samples in the Soil Survey of Kent and Surrey they were carrying out. They used a cylindrical auger one foot long, two inches

in diameter, with a slot one inch in breadth, the sides of the slot, and the bottom of the cylinder being each sharpened to a cutting edge. The worm auger was only used for exploring the subsoil to some depth. The auger was undoubtedly most useful for securing a fair sample, especially in field work, where one did not want to be burdened with a great weight of soil; but there were many soils on which it could not be used, they were either too hard, too stony, or too loose to remain in the tool. The steel box employed at Rothamsted could be made to give the most accurate results, but it was not wise to lay down any hard and fast rule as to which was the best tool. The analyst must examine the soil, and then use his judgment.

As to Dr. Leather's figures, not only did they support his opinion that fair samples could be drawn with the auger, but they showed that he must have been working with an extremely uniform soil, probably of alluvial origin. In England samples taken from adjoining fields on the same formation would vary between far wider limits than those shown by Dr. Leather's figures.

Dr. LEATHER, in reply, said that so far as stones are concerned, the determination of their amount would naturally demand that comparatively large portions of soil should be taken, but this consideration would not apply to the examination of the fine earth. Of the Indian soils examined, that at Cawnpore is alluvial, but the geological history of the Poona land is uncertain.

*83. "Some excessively saline Indian well waters." By J. W. Leather.

The composition of some well waters from the Muttra District, United Provinces, India, was given in detail. These waters contain from 200 to 2000 parts of salt per 100,000 of water. About one-half of the saline matter consists of sodium chloride; the amount of carbonate is about 20 to 30 parts; the nitrate varies from nothing to 250 parts; very large amounts of sulphate were present in some of the samples. In three cases, there was an excess of lime over that required to combine with the nitric, carbonic, and sulphuric acids, thus proving the presence of calcium chloride.

Some of these waters are used for irrigating crops. The soil of the district is open, the drainage conditions are good, and no salts accumulate in the surface soil. These waters provide an indication therefore of the maximum strength of solutions in which plants can grow, a point which is of importance in connection with the alkali lands of America, and the Usar lands of India. It is found practically that, of these well waters, those may be employed for irrigating crops which

do not contain much more than about 500 parts of salts per 100,000, or 0·5 per cent.

The amount of salts in Usar or alkali land is usually stated in parts in 100 of soil, and it is found in practice that soils containing much more than 0·1 per cent. are infertile. Immediately after irrigation, such a soil would contain a solution of about 0·33 of salts per 100 of water, but after the lapse of a few days, the proportion of water decreases to 10 or 15 per cent., and in this state the above mentioned solution would become concentrated to about 1·0 or 0·66 per cent. respectively. These figures correspond practically with what is known about the well waters.

Discussion.

Mr. J. Spiller said that in the year 1865 he had occasion to examine some remarkable products obtained from a highly saline spring which discharged itself into Lake Lohhar, India. The water left on evaporation 8·25 per cent. of solid residue, which consisted roughly of two parts of common salt to one of sodium carbonate. A local attempt at a separation of these resulted in a purified product, which had the following composition :—

Sodium carbonate	75·0
„ chloride	0·6
Calcium carbonate	1·9
Sand and ferric oxide	2·7
Water, nearly	20·0

There was no sulphate, bromide, borate, or nitrate.

***84. "Nitrobromo-derivatives of fluorescein." By J. T. Hewitt and A. W. G. Woodforde.**

The non-fluorescence of alkaline solutions of nitro-derivatives of fluorescein was explained by the assumption that the alkaline salts of orthonitrophenols have the metal attached to the nitroxyl and not to the hydroxyl group (Hewitt and Perkins, *Trans.*, 1900, **77**, 1324). With regard to the position of the nitro-groups in dinitrofluorescein, it was assumed that these occupied positions 2 and 7. (The numbering of the fluoran ring corresponds to Richter's numbering in the xanthene nucleus.)

Additional support was lent to this view by the isolation from the product of alkaline fusion of a small amount of material having a melting point of 114°. Since 4-nitroresorcin melts at 115°, the substances were supposed to be identical, and hence positions 2 and 7 were assigned to the nitro-groups in the fluoran nucleus. It is now shown,

however, that this view must be discarded; by adopting suitable precautions, 2-nitroresorcin may be isolated in considerable quantity, as had been previously demonstrated by Matras; the authors' thanks are due to M. Reverdin of Geneva for calling their attention to this work.

Dinitrofluorescein is thus 4:5-dinitrofluorescein; acted on by bromine, 4:5-dinitro-2:7-dibromofluorescein results. This substance closely resembles the original dinitrofluorescein, it dissolves in alkalis with a brown colour, but on warming a blue solution is obtained from which acids precipitate the hydrate $C_6H_4\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}C[C_6HBr(NO_2)(OH)_2]_2\\CO\cdot O\end{matrix}$.

4:5-Dinitro-2:7-dibromofluorescein has been further characterised by its *diacetyl* derivative, $C_{20}H_6Br_2N_2O_9(C_2H_3O)_2$, m. p. 276°; *dibenzoyl* derivative, $C_{20}H_6Br_2N_2O_9(C_7H_5O)_2$, m. p. 315°; *sodium* salt, $C_{20}H_6Br_2N_2O_9Na_2,2H_2O$.

Dibromofluorescein, $C_{20}H_{10}Br_2O_5$, obtained by Bayer by the limited action of bromine on fluorescein, is evidently also a 4:5-substitution derivative, since nitric acid produces from it a dinitro-derivative quite distinct from the 4:5-dinitro-2:7-dibromo-compound. The *benzoyl* derivative, $C_{20}H_8Br_2O_5(C_7H_5O)_2$, melts at 240—244°. 2:7-*Dinitro*-4:5-*dibromofluorescein* may be obtained either by the action of nitric acid upon 2:7-dibromofluorescein or of bromine upon 2:4:5:7-tetranitrofluorescein. This substance dissolves in alkalis with a magnificent purple colour not altered by boiling. Nitro-groups only render the pyrone ring unstable if in the ortho-position relatively to its oxygen atom; this is also shown by the action of ammonia, which reacts with 4:5-dinitro-2:7-dibromofluorescein, apparently in a similar manner to that observed by Reverdin in the case of dinitrofluorescein, whilst with 2:7-dinitro-4:5-dibromofluorescein it merely produces an ammonium salt.

The *diacetyl* derivative, m. p. 215°, *dibenzoyl* derivative, m. p. 301°, and *sodium* salt of 2:7-dinitro-4:5-dibromofluorescein have been prepared.

85. "On phosphorus sesquisulphide and its behaviour with Mitscherlich's test." By E. G. Clayton, F.I.C.

Many compounds of phosphorus and sulphur have been described, but of these the only one which has received any application on the large scale is the sesquisulphide, P_4S_3, discovered by Lemoine in 1864. When pure, it is a lemon-yellow, crystalline solid, with a strong odour of hydrogen sulphide, soluble at 15° in 1·6 parts of carbon bisulphide, and igniting in the air at about 100°. Commercially, several qualities of this substance are manufactured. Amongst those which have come under observation have been a coarsely granular, lemon-yellow

powder; a fine-grained, yellow powder of somewhat duller tint; and a grey product, sometimes very impure. The following are typical analyses:

	A. Yellow (fine-grained).	B. Yellow (fine-grained).	C. Yellow (coarse-grained).	D. Grey (finely granular).
Water and volatile matter (loss at 100°, in an atmosphere of carbon dioxide)	0·19	0·18	8·74	7·31
Phosphorus sesquisulphide, P_4S_3	97·86	97·62	84·95	83·34
Red phosphorus	—	—	—	1·81
Phosphoric acid, H_3PO_4	1·30	1·63	2·14	1·23
Sulphur, uncombined (soluble in carbon bisulphide)	—	—	4·17	—
Sulphur, uncombined (insoluble in carbon dioxide)	0·46	0·40	—	0·17
Calcium phosphate	—	—	—	3·35
Calcium sulphate	—	—	—	0·27
Iron oxide, &c.	—	—	—	1·72
Siliceous matter	0·19	0·17	—	0·80
	100·00	100·00	100·00	100·00
Temperature at which the specimen became luminous in the dark	92°	93°	—	58°
Temperature of ignition	94	96	86°	72
Reaction with Mitscherlich's test	negative	negative	distinct	distinct

Mörner has recently stated (*Svensk Farmaceutisk-Tidskrift*, 1901, 12, 177) that phosphorus sesquisulphide gives "more or less positive results" with Mitscherlich's test for phosphorus. The author has examined various specimens of commercial phosphorus sesquisulphide, and applied Mitscherlich's test to each in the following way: 20 grams of the compounds were distilled with 100 c.c. of 10 per cent. sulphuric acid, in an egg-shaped flask connected with a spiral condenser, the operation being conducted in a dark room. The very small amount of light emitted by the lamp was screened from the condenser and receiver, which were in complete darkness. In each case, 40 c.c. of liquid were distilled over. The results with comparatively pure specimens, such as A and B, were absolutely negative, not the faintest luminosity being perceptible in any part of the apparatus. It is evident that pure, or even approximately pure, phosphorus sesquisulphide gives no reaction with Mitscherlich's test, and that Mörner's results were obtained with samples containing small quantities of phosphorus, or of phosphorous oxide. Very crude specimens of phosphorus sesquisulphide

no doubt occasionally give Mitscherlich's reaction: thus, with the impure specimen, D (tested after being kept for many months in the laboratory), a distinct luminous cloud played about the exit of the condenser, and in the air of the receiver above the surface of the distillate, which had a faint odour of phosphorous oxide. The sample C, which had been kept for nearly three years, and had undergone considerable oxidation, being quite moist, also gave a decided reaction. The distillate from this also smelt distinctly of phosphorous oxide. The specimens A and B, which gave negative results, had been recently made. Even in these samples some oxidation had occurred, but apparently no phosphorous oxide was present. The author is now conducting some experiments with the object of discovering whether exposure and keeping can so induce partial oxidation in, or alter the composition of, pure, or nearly pure, phosphorus sesquisulphide as to impart to it after a time the property of giving Mitscherlich's reaction. Apart from its scientific interest, the point was of considerable practical importance. Meanwhile, the absence both of free phosphorus and of phosphorous oxide from phosphorus sesquisulphide of fair quality and purity and comparatively recent manufacture was clearly indicated by the negative reaction with Mitscherlich's test, and the following circumstances were corroborative as far as they went. Phosphorus sesquisulphide may be subjected to friction in air at a temperature very considerably exceeding the ignition point of phosphorus without becoming luminous, and with a total absence of "phosphorus fume"; it neither ignites nor begins to glow in the dark until a temperature of 92—96° is reached, and the finely divided residue of a solution in carbon bisulphide, evaporated on filter-paper at the ordinary temperature, neither glows in the dark, fumes, nor ignites spontaneously.

86. "Atomic and molecular heats of fusion." By P. W. Robertson.

No satisfactory relationship has hitherto been found connecting the latent heat of fusion of substances with their atomic or molecular weights. In the case of the elements, the following is shown to yield satisfactory results. "For the elements with atomic weights above 40 which do not expand on freezing, the atomic heat of fusion divided by the melting point on the absolute scale into the cube-root of the atomic volume is a constant." That is, $Aw/T\sqrt[3]{V} =$ constant.

The numbers have a mean variation of ± 10 per cent. The only exception is lead, for which the value of the expression is 25 per cent. below the mean.

In the case of the binary inorganic compounds also, the expression $Mw/T\sqrt[3]{V}$, where V is the specific volume of the solid, yields concordant

results. The values of the expression for organic compounds increase with the number of atoms in the molecule, but when compounds of similar constitution are considered, fairly constant results are obtained.

To test these relations, the latent heats of the following substances were determined :

Thallium	= 7·2	Phenanthrene	= 25
Lead	= 6·45	Phenylacetic acid	= 32
Tin	= 14·05	Tribromophenol	= 13·4
Dinitrobenzene	= 29·0	Tribromoaniline	= 14·4
	Thiosinamine = 33·4.		

87. "The preparation of mixed ketones by heating the mixed calcium salts of organic acids." By E. B. Ludlam.

A device for preparing a simple ketone from the calcium salt of the corresponding organic acid was described by Young (*Trans.*, 1891, 59, 623), which consisted in decomposing the salt at the temperature of boiling sulphur and removing the products by a stream of carbon dioxide.

The author has extended the method to mixtures of calcium salts with very satisfactory results.

The conclusions arrived at are : (i) That the decomposition is not of one molecule, but of two. (ii) There is a greater tendency towards the production of the mixed than of the simple ketone. (iii) That, for economy, it is advisable to distil the more expensive salt with excess of the cheaper one. By so doing the yield of mixed ketone from a given weight of the expensive salt is increased.

88. "Isomeric additive products of methyl, ethyl, and propyl benzyl ketone with benzylidene aniline. Part IV." By F. E. Francis and E. B. Ludlam.

The benzylideneaniline additive products of methyl, ethyl, and propyl benzyl ketones were prepared in the expectation that they would furnish evidence as to the constitution of the tautomeric forms which such compounds are capable of assuming. Methyl benzyl ketone contains the group $CH_3 \cdot CO \cdot CH_2-$, which in ethyl acetoacetate gives rise to the tautomeric form $CH_3 \cdot C(OH) : CH-$, and it was hoped that the work would have contributed to the solution of the problem of the constitution of the tautomeric forms of that compound.

Methyl benzyl ketone gave with benzylideneaniline an additive product melting constantly at 173° (a). This, under the influence of piperidine, gave the β-modification melting at 182°, and another modi-

fication melting at 184° when subjected to the action of a trace of sodium ethoxide. The hydrochloride of the α-modification was unstable; it gave no fixed melting point, but slowly decomposed between 140° and 190°. Propyl benzyl ketone gave a similar α-product, crystallising in silky needles melting at 136°, rising to 142° under the influence of piperidine, and to 143° with sodium ethoxide. Ethyl benzyl ketone gave an α-product melting at 161°, intermediate between 136° and 173°. Neither the original ketones nor any of the additive products gave any coloration with ferric chloride, and the melting points of the β- and γ-varieties fell when they were recrystallised from pure benzene. They were thus too unstable to serve the purpose for which they were prepared.

89. "The influence of solvents on the rotation of optically active compounds. Part III. Influence of benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene on the rotation of ethyl tartrate." By T. S. Patterson.

It was found that in dilute solution the influence of benzene is to lower slightly the specific rotation of the dissolved ethyl tartrate. Toluene has a greater influence of the same kind, and this influence becomes greater and greater in the other solvents in the order in which they are placed above.

It was found also that in benzene, toluene, *o*-xylene, and *m*-xylene there exists, not only a concentration of minimum rotation, but also one of maximum rotation, which lies at a greater dilution. The concentration-rotation curves for *p*-xylene and mesitylene show only a point of inflection.

The relationship between molecular-solution-volume and rotation has been investigated, and it was found that in general, although not without exception, the behaviour was the same as in the monohydric alcohols; when the dissolved ethyl tartrate has a molecular-solution-volume greater than the molecular-volume of the pure ester the rotation is correspondingly low.

The relationships between rotation, latent heat of vaporisation of the solvent, and surface tension of the solvent were also discussed.

90. "The influence of solvents on the rotation of optically active compounds. Part IV. Influence of naphthalene on the rotation of ethyl tartrate." By T. S. Patterson.

Naphthalene was found to differ greatly in its behaviour from the benzene hydrocarbons. It has the effect of greatly increasing the

rotation of the dissolved ethyl tartrate, and its influence is similar to that of water in this respect as well as in the effect of temperature change.

Thursday, June 5th, 1902. Professor THORPE, C.B., F.R.S., Vice-President, in the chair.

Messrs. Steel, F. King, S. King, West, and F. M. Perkin were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Edgar Leeder Edlin, B.A., Marsh Parade, Newcastle, Staffs.
George Felix Dudbridge Green, 9, Ross Road, South Norwood, S.E.
Arthur Francis Hosking, Roskear Villas, Camborne, Cornwall.
Douglas K. Jardine, B.Sc., 20, Doune Terrace, Kelvinside, Glasgow.
Leonard Smith, 14, West Hill, Highgate, N.

The certificate of Mr. Herbert Purtan, London Chambers, Durban, Natal, authorised by the Council under Bye-law I (3) was read.

Of the following papers, those marked * were read:—

***91. "The action of ungerminated barley diastase on starch. Part I.' By J. L. Baker.**

When the diastase from ungerminated barley is allowed to act at 50° on a solution of soluble starch, hydrolysis proceeds until at the end of an hour to an hour and a half the constants of the dissolved matter are $[\alpha]_{D3\cdot93} = 160—165°$ and $R_{3\cdot93} = 60—65°$. After this the reaction is a comparatively slow one, and if continued for 96 hours the reducing power is only increased to $R_{3\cdot93} = 70$, the iodine reaction being still blue.

An examination of the products, after the reaction had proceeded for $1\frac{1}{2}$ to 2 hours, showed that a dextrin and maltose were the sole products. After 24 hours, evidence of the presence of glucose was obtained, the amount of this sugar apparently increasing in proportion to the time of conversion.

The dextrin, isolated by precipitation with alcohol from the products of the conversion, gave a blue iodine reaction, a specific rotation of $[\alpha]_{D3\cdot93} = 190—195°$, and a reducing power of $R_{3\cdot93} = 0\cdot55—1°$. The alcoholic solutions from which the dextrin was precipitated were col-

lected and examined and found to contain maltose, glucose if the conversion period was prolonged, but no trace of any dextrin of less complexity than described above.

Barley diastase acts on the above-mentioned dextrin very slowly, the constants of the solution after 90 hours at 45—50° being $[\alpha]_{D3\cdot93} = 160°$ and $R_{3\cdot93} = 32°$. The products, which give a blue iodine reaction, consist of maltose, unaltered dextrin, and glucose. The presence of glucose could be detected in 18 hours, but after 90 hours the amount formed had only slightly increased. The action of malt diastase on this dextrin was more vigorous. After 18 hours at 55° the solution, which no longer gave an iodine reaction, had the constants $[\alpha]_{D3\cdot93} = 149\cdot3°$ and $R_{3\cdot93} = 50—51°$. An examination of the products showed that they consisted of maltose, a mixture of achroo-dextrins, and a considerable quantity of glucose.

Since barley diastase is without action on maltose, the glucose found in the products from the prolonged action of barley diastase on soluble starch must be derived from the dextrin. Barley diastase completely liquefies starch paste in 2 to 3 hours at 50°, the products consisting of the above described dextrin and maltose.

The dextrin obtained by the action of barley diastase on soluble starch or starch paste differs markedly from Nageli's "amylodextrin," which was reinvestigated by Brown and Morris (Trans., 1889, **55**, 449). In consideration of its general behaviour and close relation to the parent substance starch, the author proposes to term the new dextrin *α-amylodextrin*.

Discussion.

Mr. A. R. Ling asked if the author had continued the reaction between barley diastase and soluble starch solution for a longer period than 144 hours, in fact until (when working with an excess of the diastase) the final point was reached. It had recently been shown by Mr. B. F. Davis and himself that by the action of the diastase from air-dried malt on starch paste below 60°, the whole of the starch was converted into maltose in 40 hours. He had been struck by Mr. Baker's observation that maltose was practically the sole cupric-reducing compound formed in the early stages of the reaction between barley diastase and starch solution. With regard to the dextrin which the author had named α-amylodextrin, and which gave a blue iodine reaction, he could not help thinking, in view of what was known of starch-conversion products, that this dextrin (despite its apparent stability towards barley diastase) must have contained soluble starch. An indication of this was afforded by the behaviour of the dextrin towards malt diastase when the iodine reaction vanished.

Mr. Baker, in reply, said that with regard to the suggestion of Mr.

Ling and Dr. Thorne, that α-amylodextrin was a mixture of another dextrin and unaltered soluble starch, he was convinced that α-amylodextrin was an entity, from the fact that when this dextrin was acted on by barley diastase for 18 hours at 50°, it split up into maltose and unaltered α-amylodextrin. If this residual α-amylodextrin was then subjected to the action of barley diastase under similar conditions, the same products were formed. This treatment had been repeated many times, and it did not seem possible that under such circumstances, soluble starch could escape the action of barley diastase.

***92. "The decomposition of chlorates. Part V. Potassium chlorate in presence of oxides of manganese, and the theory of perchlorate formation." By W. H. Sodeau, B.Sc.**

In continuation of the previous work of the author, it was now shown that the amount of chlorine accompanying the oxygen evolved from potassium chlorate in presence of oxides of manganese was not increased on reducing the pressure under which the decomposition took place, whilst secondary reactions removing free chlorine from gaseous products have previously (*Trans.*, 1901, **79**, 251) been experimentally shown to be greatly decreased on decomposition under reduced pressure. It was thus seen that no such secondary reaction occurred in the present case.

This excludes all theories which assume the cycle of changes to include the formation of a compound containing manganese and chlorine or potassium and manganese, such as McLeod's well known theory. Oxygen being the only remaining constituent, it followed from this process of exclusion that the cycle of changes brought about by addition of oxides of manganese was confined to alternate oxidation and deoxidation (like the decomposition of hydrogen peroxide in presence of the same substances). It is probable that the formation of potassium perchlorate during the decomposition of the pure chlorate by heat was due to an exothermic reaction independent of that which yielded chloride and oxygen. The non-production of perchlorate seemed to be the natural result of the addition of a substance (manganese dioxide) which brings about the transformation into chloride and oxygen at a temperature far below that at which the chlorate begins to give chloride and perchlorate.

Discussion.

Professor E. J. Mills said that, in association with Mr. Stevenson, he had, some years ago, investigated the action of manganic oxide on potassic chlorate. They had not been able to find or prepare an oxide free from constitutional water, and any attempt to render the oxide an-

hydrous resulted in a loss of oxygen. Eventually, they used the oxide of Beilstein and Javorsky. Their work had reference chiefly to the question of catalysis, and they found that small quantities acted in proportion more energetically than large ones. It should be borne in mind that the composition of hot manganic oxide was affected by pressure. Altogether, it was a question whether the numerous difficulties besetting the investigation could be satisfactorily surmounted.

Mr. SODEAU, in reply, stated that in his examinations of the aqueous extracts of the residues, phenolphthalein was employed with precautions against carbon dioxide, and a very small fraction of the amount of alkalinity found by Prof. McLeod would therefore have been detected. The extracts were actually slightly acid, and the residual manganese peroxide rapidly absorbed potash from solution.

***93. "Studies in the tetrahydronaphthalene series. I. The diazoamino-compounds of *ar*-tetrahydro-β-naphthalene." By C. Smith, B.Sc.**

It has been shown by Bamberger and Bordt (*Ber.*, 1889, **22**, 625) that *ar*-tetrahydro-α-naphthylamine combines with diazonium salts, yielding azo-compounds.

The experiments of the author prove that *ar*-tetrahydro-β-naphthylamine behaves like a benzenoid amine and yields diazoamino-compounds.

The following compounds have been prepared and examined: p-*Toluenediazoaminotetrahydro-β-naphthalene*, $CH_3 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_{10}H_{11}$, yellow crystals, m. p. 107°; readily soluble in alcohol and benzene, sparingly in petroleum. o-*Nitrobenzenediazoaminotetrahydro-β-naphthalene*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_{10}H_{11}$, orange-yellow crystals, m. p. 134°. p-*Nitrobenzenediazoaminotetrahydro-β-naphthalene*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_{10}H_{11}$, well-defined chocolate-brown crystals, melting at 179° with violent decomposition. p-*Bromobenzenediazoaminotetrahydro-β-naphthalene*, $Br \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_{10}H_{11}$, crystallises in lemon-yellow needles which decompose slightly on exposure to the air and melt at 134°. *Diazoaminotetrahydro-β-naphthalene*, $C_{10}H_{11} \cdot N_2 \cdot NH \cdot C_{10}H_{11}$, well-defined, amber coloured crystals; m. p. 104°. *β-Naphthalenediazoaminotetrahydro-β-naphthalene*, $C_{10}H_7 \cdot N_2 \cdot NH \cdot C_{10}H_{11}$, crystallises in light yellow, lustrous plates, m. p. 137·5°. *Tetrahydro-β-naphthaleneazo-β-naphthylamine*, $C_{10}H_{11} \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$, dark-red, lustrous crystals moderately soluble in hot alcohol; m. p. 130°. *Tetrahydro-β-naphthaleneazo-β-naphthol*, $C_{10}H_{11} \cdot N_2 \cdot C_{10}H_6 \cdot OH$, vermilion-red crystals with a green shimmer, m. p. 153°; it is insoluble in sodium hydroxide, and only sparingly soluble in hot alcohol.

Discussion.

Dr. Morgan pointed out that the mixed diazoamines of the tetrahydronaphthalene series are members of an extensive series of diazoamino-compounds having the general formula XN_3HY, which can be produced from one or other of the two pairs of generators, XN_2Cl,YNH_2 and YN_2Cl,XNH_2, where X and Y are dissimilar aromatic nuclei derived from benzene, naphthalene (*Trans.*, 1902, **81**, 90), and tetrahydronaphthalene.

The genesis of these substances and their decomposition with mineral acids justify the belief that they are solid solutions of the two compounds, $XN_2{\cdot}NHY$ and $YN_2{\cdot}NHX$.

***94. "Experiments on phosphorus tetroxide." By C. A. West, B.Sc.**

The author gave an account of the preparation of phosphorus tetroxide and of his attempts to determine its molecular weight. Methods based upon observation of the freezing or boiling points of a solution could not be used, no suitable solvent being found. At a red heat, under atmospheric pressure, the compound does not volatilise rapidly enough to allow of the determination of vapour density, but four concordant experiments at about 1400° led to the unexpected conclusion that the molecular formula is P_8O_{16}, that is, twice what would have been expected from comparison with P_4O_6 and P_4O_{10}.

Some new determinations of the vapour density of phosphoric oxide at this temperature were also made. The mean of six concordant results gave 300·4 for the molecular weight, P_4O_{10} requiring 284.

95. "The decomposition of compounds of selenium and tellurium by moulds and its influence on the biological test for arsenic." By O. Rosenheim, Ph.D.

A paper has recently been published (Maassen, *Arb. Kais. Ges. A.*, 1902, **18**, 475) on the biological test for arsenic and the formation of organic compounds of arsenic, selenium, and tellurium by moulds. The author has been occupied for some time on the same subject in its connection with the detection of arsenic in beer and sugar, and had intended to publish his results in a more complete form. In view of Maassen's publication it has, however, been thought advisable to give a short *résumé* of the results in this direction confirming those of Maassen.

The biological test for arsenic (Gosio, *Ber.*, 1897, **30**, 1024) is said to be characteristic of this substance (Abel and Buttenberg, *Z. Hyg.*, 1899, **32**, 449). The test consists in the formation of gaseous organic

arsenic compounds, possessing a characteristic garlic odour, produced by the vigorous growth of certain moulds (*Aspergillus*, *Mucor*, and *Penicillium*) in media containing arsenic, and permits of its detection where chemical methods fail. When applying this test to certain substances (beer and sugar) which contained selenium and arsenic, the author noticed a pronounced fæcal odour different from that produced by arsenic alone. It was thought that this was due to the presence of selenium, and experiments with soluble selenium compounds confirmed this view. It was also found that tellurium compounds were decomposed by *Penicillium brevicaule*, giving rise to the production of a very characteristic odour. Owing to the extreme sensitiveness of the test with regard to arsenic, it was thought necessary to employ absolutely pure compounds of selenium and tellurium. The odour produced by the decomposition of selenium compounds is of a very disagreeable character (somewhat like skatol or mercaptan), whilst the gases formed by tellurium compounds possess a pronounced garlic odour. The test is extremely sensitive: 0·01 mg. in 1 c.c. of liquid is easily demonstrated by a vigorous growth of the mould. Unlike arsenic, pure selenium and tellurium are not attacked by the mould. It was found best to perform the test by using the medium proposed by Abel and Buttenberg (*loc. cit.*), namely, sterilised bread-crumbs, to which the sterilised liquid in question is added after infection with the mould.

The author has drawn attention elsewhere (*Chem. News*, 1901, **83**, 277) to the influence of selenium on certain chemical tests for arsenic, and it is evident from the above results that in applying the biological test for arsenic, it is also necessary to take the possible presence of selenium (and tellurium) into consideration.

96. "Constituents of Gambier and Acacia catechus." By A. G. Perkin and E. Yoshitake.

The short paper on catechin, just published (Kostanecki and Tambor, *Ber.*, 1902, **35**, 1867), renders it necessary to give the results of an investigation which has been in progress for more than two years. The gambier catechu employed has been found to contain two catechins (*b*) and (*c*), and a third (*a*) has been isolated from the acacia catechu.

Catechin (*b*), $C_{15}H_{14}O_6,4H_2O$, air-dried, colourless needles, corresponds in its melting point, 175—177°, with Gautier's (*b*) catechin (*Bull.*, 1879, **30**, 567), and gives, on fusion with alkali, phloroglucinol, protocatechuic acid, and an acid resembling acetic acid. The *disazobenzene* compound (compare Etti, *Monats.*, 1881, **2**, 552), $C_{15}H_{12}O_6(C_6H_5N_2)_2$, salmon-red needles, m. p. 193—195°; its *triacetyl* derivative, $C_{15}H_9O_6(C_6H_5N_2)_2(C_2H_3O)_3$, orange-red needles, m. p. 253—255°;

pentabenzoyl catechin, $C_{15}H_7O_6(C_7H_5O)_5$, colourless needles, m. p. 151—153°, and *tetrabenzoyl* catechin, prismatic needles, m. p. 171—172°, have been studied. Molecular weight determinations by the cryoscopic method of the two latter compounds confirm these formulæ.

Catechin (*c*), $C_{15}H_{14}O_6$, air-dried, contains no water of crystallisation, and forms colourless prisms, m. p. 235—237°. It yields an *azobenzene* compound, $C_{15}H_{12}O_6(C_6H_5N_2)_2$, orange-red needles, m. p. 215—217°, the *acetyl* derivative of which melts at 250—253°, and on fusion with alkali gives phloroglucinol and protocatechuic acid. It has been found at present only in minute quantity.

Catechin (*a*), $C_{15}H_{14}O_6,3H_2O$ (or less probably $C_{14}H_{14}O_6,3H_2O$) air-dried, forms colourless needles and corresponds in its melting point, 204—205°, with Gautier's (*a*) catechin. Molecular weight determinations of the *pentabenzoyl* derivative (prismatic needles, m. p. 181—183°) coincide with this formula. The *azobenzene* compound, $C_{15}H_{12}O_6(C_6H_5N_2)_2$, needles, m. p. 198—200°, gives a *triacetyl* derivative, $C_{15}H_9O_6(C_6H_5N_2)_2(C_2H_3O)_3$, orange-red leaflets, m. p. 227—229°. Fusion with alkali gave phloroglucinol, protocatechuic acid, and an acid resembling acetic acid.

Cyanomaclurin (*Trans.*, 1895, 67, 939), a constituent of *Artocarpus integrifolia*, has been found to contain a phloroglucinol group and is probably isomeric with these catechins.

97. "The decomposition of oxalacetic hydrazone in aqueous and acid solution, and a new method of determining the concentration of hydrogen ions in solution." By H. O. Jones and O. W. Richardson.

When oxalacetic hydrazone is heated with dilute acids it gives rise simultaneously to pyruvic hydrazone and carboxylic dioxide and to pyrazolone carboxylic acid and water (Fenton and Jones, *Trans.*, 1901, 79, 92), the amounts of the former products being in the inverse order of the concentrations of the hydrogen ions in the solutions used. The hypothesis suggested to explain these observations was that the negative ion of the oxalacetic hydrazone underwent the first of the above decompositions when heated, whereas the undissociated molecule underwent the second.

Experiment shows that the results are better explained by supposing that the rate of decomposition into pyruvic hydrazone is proportional to the concentration of oxalacetic hydrazone, whereas the rate of formation of the pyrazolone carboxylic acid is jointly proportional to the concentration of the original substance and of the hydrogen ions.

The reaction was investigated in two ways, first the rate of evolution of carbon dioxide at a constant temperature (about 80°) was

determined, and, secondly, the total amount of carbon dioxide given off at 100° was determined, in both cases water and sulphuric acid of different strengths being used. The results obtained agree with the requirements of the second hypothesis.

According to both theories, the amount of carbon dioxide produced satisfies the following equation, $\log\left[\frac{1}{1-\frac{C_2}{[C_2]_\infty}}\right]=\beta t$, where C_2 = concentration of pyruvic hydrazone (or amount of carbon dioxide evolved) at any time t, $[C_2]_\infty$ its final concentration, and β = a constant.

The hypothesis of the decomposition of the negative ion requires that β should decrease with increasing concentration of hydrogen ions, whereas the view here put forward requires that β should increase. Now it was found that β did increase with increasing concentration of hydrogen ions. This forms a crucial test between the two views.

A quick and easy method for determining the concentration of hydrogen ions in solution has also been worked out and tested.

Experiments have been made with the *p*-bromophenyl hydrazone of oxalacetic acid which decomposes in a similar way, and the results show satisfactory agreement with requirements of the theory stated above.

98. "The dissociation constants of oxalacetic acid and its hydrazone." By H. O. Jones and O. W. Richardson.

The authors have determined the dissociation constants of oxalacetic acid and its phenyl hydrazone. The conductivities of solutions of these substances were determined at 25°, and from the results the following values were obtained:

For oxalacetic acid, K = 1·33. Oxalacetic hydrazone, K = 0·11.

99. "Derivatives of butyrylpyruvic acid." By A. Lapworth and A. C. O. Hann.

Certain points of interest arising out of the study of the Claissen reaction as applied to $\alpha\beta$-unsaturated ketones (*Trans.*, 1901, **79**, 1283) led the authors to study the action of ethyl oxalate and sodium on benzylidene*iso*propylmethylketone. The results were not those anticipated, but the following compounds have been prepared in the course of the work:

Benzylideneisopropylmethylketone, $CHMe_2\cdot CO\cdot CH{:}CHPh$, is an oil (b. p. 274—276°). The *oxime* melts at 131—132° and the *semicarbazone* at 166—167°.

Ethyl iso*butyrylpyruvate*, $CHMe_2\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et$, from *iso*propyl-

methylketone, ethyl oxalate, and sodium ethoxide, is a nearly colourless oil which boils and decomposes at 230—232°; it does not solidify at −15°. The *copper*, *nickel*, *calcium*, and other derivatives have been prepared. When the ester is hydrolysed with strong potassium hydroxide solution under certain conditions and the resulting solution treated with excess of strong hydrochloric acid, a sparingly soluble compound is precipitated in quadratic plates. This is an *acid potassium* iso*butyrylpyruvate* having the composition $(C_7H_{10}O_4)_3{\cdot}C_7H_9O_4K$; its solution gives a red coloration with ferric chloride, and becomes yellow on addition of excess of alkalis; it is only decomposed by a large excess of mineral acid; a similar sodium salt was not obtained.

Ethyl n-*butyrylpyruvate*, $Pr{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et$, is similar in properties to the ester described above. When it is hydrolysed with potassium hydroxide, it yields a sparingly soluble *acid potassium* n-*butyrylpyruvate* crystallising in asbestos-like needles, which has, however, the composition $(C_7H_{10}O_4)_2{\cdot}C_7H_9O_4K$. As in the former instance, this substance is very stable towards acids, and no corresponding sodium salt could be obtained.

100. "Sulphocampholenecarboxylic acid." By A. W. Harvey and A. Lapworth.

When the residues obtained by evaporating the last aqueous mother liquors in the preparation of ammonium bromocamphorsulphonate were fractionally extracted with alcohol, a small quantity of a new substance dissolved and was obtained in the form of transparent, calcite-like crystals. A small quantity of this product has also been obtained by Dr. Kipping.

The compound has the formula $C_{10}H_{15}SO_5NH_4$, and it is the hydrogen ammonium salt of an unsaturated, monocyclic, sulphocarboxylic acid, $CO_2H{\cdot}C_9H_{14}{\cdot}SO_3H$, for which the name *sulphocampholenecarboxylic acid* is proposed. That it is unsaturated is shown by its aqueous solution instantly decolorising bromine water and an ice-cold solution of potassium permanganate.

The normal *barium* and *calcium* salts, $C_{10}H_{15}SO_5Ba$ and $C_{10}H_{15}SO_5Ca$, crystallise well and are more soluble in cold than in hot water; the normal *ammonium* salt is very soluble in water. The *hydrogen barium* and *hydrogen calcium* salts crystallise in fine needles. The chloride and bromide do not crystallise readily.

When solutions of the salts are treated with bromine, a molecular proportion of the latter is at once absorbed, and a very sparingly soluble substance separates. This appears to be a sultonecarboxylic acid, $CO_2H{\cdot}C_9H_{14}Br{\cdot}SO_2{\cdot}O$; it crystallises from chloroform in small

prisms, melts and decomposes at 155°, dissolves in alkalis and alkali carbonates, and is reprecipitated unchanged by acids.

The investigation of the acid and its derivatives is in progress.

101. "Some properties of camphorquinonephenylhydrazone." By A. Lapworth and A. C. O. Hann.

It has been found by Betti (*Ber.*, 1899, 32, 1995) that camphorquinonephenylhydrazone ("camphormethylenehydrazone") usually exists as a mixture of two desmotropic forms. One of these melts at 180°, gives a reddish coloration with ferric chloride in benzene solution, and is therefore probably the enolic form, $C_8H_{14}<\begin{matrix}C\cdot N:NPh\\ \|\\ C\cdot OH\end{matrix}$. The other, melting at 155°, may be isolated by adding a trace of piperidine to a solution of the hydrazone in benzene; as it gave no distinct colour with ferric chloride, it was supposed to be the ketonic form, $C_8H_{14}<\begin{matrix}C:N\cdot NHPh\\ |\\ C:O\end{matrix}$.

With Betti's permission, the authors have carefully studied the properties of the compound, and, although they are able to confirm all his statements with regard to the enolic form, they have not been able to isolate a second modification in the pure state, although there can be no doubt that one is present; they think that the substance melting at 155° must be a mixture of both forms.

The speed with which equilibrium between the two forms, in various media, is attained was investigated by observations of the mutarotation. Equilibrium appears to be reached most rapidly in alcoholic solution, a constant rotation being observed at once. In chloroform or benzene, however, the change occurs very slowly, as in 1 per cent. solution at the ordinary temperature it occupies several days.

In benzene, with solutions varying in concentration from 0·1 to 1 per cent., the initial rotation, when the pure enol is used, is about $[\alpha]_D = +325°$, and falls to between $+205°$ and $290°$ according to the concentration. With all specimens of mixed material, even when prepared by Betti's method, a fall was invariably observed in dilute solution, indicating that the enol was still present in considerable amount.

The effect of catalytic agents on the rate of change in benzene was carefully studied. Traces of bases, if not too weak, whether primary, secondary, or tertiary, accelerate the change, and, amongst others, ammonia, aniline, piperidine, pyridine, brucine, and strychnine were tried and found to be effective. Acids, on the other hand, retard the change, and it is possible to arrest the fall in rotation at any point desired by the addition of a minute quantity of trichloroacetic acid, when it will again proceed on addition of a trace of a base.

In all cases, as was to be expected, the state of equilibrium was found to be independent of the catalytic agent.

102. "Optically active esters of β-ketonic and β-aldehydic acids. Part I. Menthyl hydroxymethylenephenylacetate." By A. Lapworth and A. C. O. Hann.

The authors propose to investigate certain aspects of the question of tautomerism involving the migration of hydrogen atoms by the employment of esters of β-ketonic and β-aldehydic acids with optically active alcohols of high molecular weight. It is hoped that the compounds may thus be obtained in a crystalline and, therefore, more easily purified form, and that by observation of the change of rotation, further evidence with regard to certain obscure points may be obtained.

Menthyl hydroxymethylenephenylacetate, $HO\cdot C{:}CPh\cdot CO_2C_{10}H_{19}$, may be prepared by the action of sodium on a mixture of menthyl phenylacetate and formate dissolved in anhydrous ether. It is precipitated from the aqueous solution of its sodium derivative on addition of acids as an oil which rapidly soldifies, and crystallises from light petroleum in transparent prisms or pyramids, which belong to the tetragonal system. These melt at 82—83° and exhibit triboluminescence, which is sufficiently brilliant to be observed in broad daylight. Its freshly prepared 2 per cent. solution in chloroform has $[\alpha]_D = -74{\cdot}6°$; this falls in a few days to about −71°. In absolute alcohol, the rotation is $[\alpha]_D = -64{\cdot}9°$, and falls only slightly, if at all, in course of time. Although its alcoholic solution is rapidly coloured violet by ferric chloride, its solution in ether or benzene is not affected unless it is boiled with the salt for some time, or a trace of a base is added, when a similar coloration develops. The solid probably represents the aldehydic form of the ester (Wislicenus, *Ann.*, 1900, **312**, 34).

The *copper* derivative crystallises in green prisms which melt and decompose at 92—95°; the *sodium* derivative forms thin, transparent plates.

The *phenylcarbamate*, $NHPh\cdot CO_2\cdot CH{:}CPh\cdot CO_2\cdot C_{10}H_{19}$, crystallises in long, slender needles melting and decomposing at 235—237°. The *acetate*, $AcO\cdot CH{:}CPh\cdot CO_2\cdot C_{10}H_{19}$, separates from ethyl acetate in needles melting at 51—52°.

The oxime is immediately precipitated as an oil on mixing solutions of the ester with one of free hydroxylamine or hydroxylamine acetate. With phenylhydrazine, the ester is converted into the diphenylpyrazolone which is obtained from the corresponding ethyl ester.

The enolic modification of the ester appears to be very unstable, and under conditions in which the liquid enolic ethyl ester may be obtained, the above compound was always produced. No evidence of the existence of isomeric copper or acetyl derivatives could be obtained.

103. "Optically active esters of β-ketonic and β-aldehydic acids Part II. Menthyl acetoacetate." By A. Lapworth and A. C. O. Hann.

Menthyl acetoacetate may be obtained in small quantity by the action of sodium on menthyl acetate, but is far more easily prepared by heating menthol with ethyl acetoacetate until alcohol ceases to come off. These observations were made before the authors were aware that Cohn had prepared the ester by the latter process (*Monatsh.*, 1900, 21,200—204). As Cohn has since notified (*Ber.*, 1900, 33, 734) that he had abandoned the work, with his concurrence the authors have resumed the study of this substance and its derivatives.

The compound may be obtained in large, lustrous, probably monoclinic prisms which the authors believe to represent the ketonic form. Its rotation in 2 per cent. solution in benzene is initially about $[\alpha]_D = -61—62°$ but slowly increases to about $-68°$, owing doubtless to partial conversion into the enolic form; similar changes are observed when it is dissolved in chloroform, light petroleum, and dry ethyl acetate. The duration of the change varies greatly with the purity of the solvent, as the compound is exceedingly sensitive to catalytic agents. As usual, all bases accelerate the change, and the mutarotation, unlike that of camphorquinonehydrazone, and of nitrocamphor is accelerated by traces of acids also. Equilibrium between the two forms appears to be attained almost at once in alcohol, practically no alteration of rotation with time being noticeable.

The *copper* derivative of the ester crystallises from alcohol in green prisms which contain alcohol; these rapidly become opaque and finally have the melting point 117—118°.

The ester readily affords a well-defined *semicarbazide*, $NH_2 \cdot CO \cdot N_2H_2 \cdot CMe{:}CH \cdot CO_2C_{10}H_{19}$, flat needles, m. p. 143—144°; in benzene $[\alpha]_D = -56{\cdot}1°$. The *p-nitrophenylhydrazide*, $C_6H_4NO_2 \cdot N_2H_2 \cdot CMe{:}CH \cdot CO_2 \cdot C_{10}H_{19}$, brilliant prisms, m. p. 105—106°; in benzene $[\alpha]_D = -42{\cdot}5°$.

Menthyl β-aminocrotonate, $NH_2 \cdot CMe{:}CH \cdot CO_2C_{10}H_{19}$, prepared by the action of gaseous ammonia; forms large, transparent plates, m. p. 88—89°; in benzene $[\alpha]_D = -105{\cdot}2°$. *Menthyl β-phenylaminocrotonate* $NHPh \cdot CMe{:}CH \cdot CO_2C_{10}H_{19}$, crystallises in flat, rectangular plates m. p. 85—86°; it has $[\alpha]_D = -98{\cdot}2°$. *Menthyl benzylaminocrotonate*, $CH_2Ph \cdot NH{:}CMe{:}CH \cdot CO_2C_{10}H_{19}$, crystallises in flat needles, m. p. 85—86°; in benzene $[\alpha]_D = -59{\cdot}8°$.

Menthyl C-*benzoylacetoacetate*, $CHBzAc \cdot CO_2C_{10}H_{19}$, is an oil; in benzene $[\alpha]_D = -44{\cdot}3°$; its *copper* derivative forms slender needles, is sparingly soluble in most media, and melts at about 230°.

Neither the oxime, the *iso*nitroso-, nor bromo-derivatives of the ester have yet been obtained in a pure condition.

The ester condenses readily with aldehydes, forming, in some cases, well crystallised compounds. Unlike ethyl acetoacetate, when condensed with benzaldehyde at the ordinary temperature by the aid of piperidine, it affords, for the most part, a monobenzylidene compound.

104. "The mechanism of simple desmotropic change." By A. Lapworth and A. C. O. Hann.

Brühl has advanced the hypothesis (*Ber.*, 1899, **32**, 2329) that enols (which are weak acids and electrolytes) are transformed into the isodynamic ketones, by a process which involves initial ionisation into hydrogen ions and organic ions or "residues," which may reunite in two ways, so that finally the ketone is produced in this manner:

$$:C=C\cdot OH \longleftrightarrow :C=\overline{C}-O+\overset{+}{H} \longrightarrow :CH-\dot{C}=O.$$

He found, as he anticipated, that the velocity of transformation of enolic ethyl mesityloxideoxalate in solution into the ketonic form increases roughly with the dielectric constant of the medium.

Although the principle here introduced appears quite reasonable, and more capable of experimental and theoretical development than any other yet suggested, it is clearly incomplete, since ketones, although apparently non-conductors, are known to exist in equilibrium with their conducting enolic forms, and the velocity of transformation must be far slower than the ionisation velocity. Since change of internal structure is necessary, and isomerisation appears to increase with ionisation, the authors think that Brühl's suggestion would lead to the following view of the processes involved in a keto-enol transformation (compare *Trans.*, 1901, **79**, 1266).

$$\left\{\begin{array}{lcl} X=Y-Z-H & \longleftrightarrow & X=Y-Z-+H \\ X=Y-Z- & \longleftrightarrow & -X-Y=Z \\ -X-Y=Z+H & \longleftrightarrow & XH-Y=Z \end{array}\right.$$

Here it appears necessary to assume that ketones themselves are very slightly ionised, which is consistent with the views of Thiele, Vorländer, and others. According to this view, bases should accelerate and acids retard the change, and the state of equilibrium should be independent of the catalytic agent, but dependent, not only on the two dissociation constants, but also on the velocities indicated in the second line. It is, in fact, perfectly consistent with the properties of certain isodynamic pairs, for example, nitro- and *iso*nitro-camphor (Lowry, *Trans.*, 1899, **75**, 221), and camphorquinonehydrazone.

However, the complete difference in behaviour of camphorquinonehydrazone and menthyl acetoacetate toward acids indicates that there

are at least two classes of substances, and that more than one type of process may go on.

To account for the action of acids in accelerating the speed of migration of a hydrogen atom, in certain cases, on a principle similar to that proposed by Brühl, it seems necessary to assume that the compounds may react as bases. Since, as before, a change of structure is involved, the change may be conventionally analysed as follows:

$$\begin{array}{lcl} X=Y-Z-H+H & \leftrightarrow & XH\dot{-}Y-Z-H \\ XH\dot{-}Y-Z-H & \leftrightarrow & XH-Y\dot{-}Z-H \\ XH-Y\dot{-}Z-H & \leftrightarrow & XH-Y=Z+H \end{array}$$

where the dot indicates the direction in which the "free affinity" of Y is temporarily disposed, a convention easily understood by reference to models.

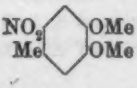
The process thus represented requires an acceleration of the change by acids, and a final state of equilibrium independent of their presence.

Clearly, a compound might react in either or possibly in both ways, according to the conditions. In nearly all cases observed, however, the first process would appear to go on, the latter being somewhat exceptional, at least as an important factor. Obviously, the state of equilibrium must be the same when attained by either process.

105. "Trimethylbrazilone." By W. H. Perkin, jun.

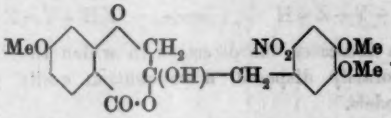
During the course of a long series of experiments on the constitution of brazilin, it was shown (W. H. Perkin and A. W. Gilbody, *Proc.*, 1899, **15**, 27) that trimethylbrazilin, $HO\cdot C_{16}H_{10}O(OMe)_3$, on oxidation with chromic acid, yields trimethylbrazilone, $HO\cdot C_{16}H_8O_2(OMe)_3$. It was also stated that nitric acid converts trimethylbrazilone into a substance crystallising in yellow needles, which dissolve in alkalis, forming an intense purple solution; this, on standing, yields besides *p*-methoxysalicylic acid, $MeO\cdot C_6H_3(OH)\cdot CO_2H$, two neutral substances melting at 118° and 206° respectively. Since the yellow substance did not give the usual qualitative tests for nitrogen, it was at first thought that it did not contain this element; subsequent quantitative experiments, however, demonstrated the presence of nitrogen, and showed that the substance has the formula $C_{19}H_{19}O_9N$. It is proposed to name it *nitrohydroxydihydrotrimethylbrazilone*.

The two neutral substances having the melting points 118° and 206° are probably isomeric, and have the formula $C_9H_{11}O_4N$, and as they each contain two methoxy-groups, they are apparently nitrodimethoxymethylbenzenes, the former (m. p. 118°) being probably identical with the compound



which has already been prepared by H. Cousin (*Ann. Chim. Phys.*, 1898, [vii], 13, 480), and which melts at 117°. There is, however, a possibility that the very sparingly soluble substance of melting point 206° has a higher molecular weight such as that represented by the formula $(C_9H_{10}NO_4)_2$.

When nitrohydroxydihydrotrimethylbrazilone is oxidised with permanganate, it yields 2-carboxy-5-methoxyphenoxyacetic acid, and since it also yields an acetyl compound, it is probably a lactone, having the formula



or some formula closely allied to it.

The author has not yet concluded his experiments on this interesting nitro-compound, but finds it necessary to publish this short note because of a recent publication of Bollina, Kostanecki, and Tambor (*Ber.*, 1902, 35, 1675), which contains a description of some experiments on this compound.

The author hopes that these chemists will allow him, for a short time longer, the uninterrupted investigation of this substance.

At the next meeting, on Wednesday, June 18th, at 5.30 p.m., there will be a ballot for the election of Fellows, and the following papers will be communicated:

"Elimination of a nitro-group on diazotisation. Dinitro-*p*-anisidine." By R. Meldola and J. V. Eyre.

"A new type of substituted nitrogen chlorides." By F. D. Chattaway.

"The colour-changes exhibited by the chlorides of cobalt and some other metals, from the standpoint of the theory of electro-affinity." By F. G. Donnan and H. Bassett, jun.

"The stereochemical formulæ of benzene." By J. E. Marsh.

"An accurate method of determining the compressibility of vapours." By B. D. Steele.

"The molecular condition of borax in solution." By H. S. Shelton.

"Preliminary notice of some new derivatives of pinene and other terpenes." By W. A. Tilden and H. Burrows.

"The preparation of pure chlorine and its behaviour towards hydrogen." By J. W. Mellor and E. J. Russell.

"The union of hydrogen and chlorine. Part V." By J. W. Mellor.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on **Wednesday, June 18th**, 1902.

Ball, James Handby,

St. Stephen's Villa, Limerick.

Analytical Chemist. B.Sc. Honours Chemistry, Victoria University. Analyst to The Condensed Milk Company of Ireland, Ltd. Past Experience. (1) Assistant to Dr. Campbell Brown. (2) Chemist to The North of England Chemical Works, Berwick-upon-Tweed. (3) Science Master of The Carpenters' Company's Technical Institute, Stratford, E., and at The Blue School, Wells, Somerset.

J. Campbell Brown. Herbert B. Stocks.
W. Collingwood Williams. Charles A. Kohn.
J. G. Taylor.

Bucknell, Edwin Thomas Holman,

Ebley House, Parsonage Street, Dursley, Glos.

Chemical Laboratory Assistant. Student in the Merchant Venturers' Technical College Laboratory (Bristol) three years. Five and a half years as Assistant in the Rugby School Chemical Laboratory.

G. Stallard. James Leicester.
J. Wertheimer. F. N. A. Fleischmann.
G. P. Darnell-Smith.

Burt, Bryce Chudleigh,

University Settlement, Bermondsey, S.E.; Univ. Coll., Gower Street.

Research Student at University College. B.Sc. (Lond.), first class hon. Chemistry. Late Student and Associate of Merchant Venturers' Coll. Bristol (four years). At present Research Student at Univ. College, London.

William Ramsay. F. G. Donnan.
Edward C. Cyril Baly. Morris W. Travers.
Alex. Findlay.

Claudet, Arthur Crozier,

27, Daleham Gardens, Hampstead, N.W.

Assayer and Metallurgist, and Analytical Chemist. Associate of the Royal School of Mines. Fellow of the Institute of Chemistry.

W. C. Roberts-Austen. John S. Sellon.
Thos. Kirke Rose. George Matthey.
A. K. Huntington.

Clough, William Thomas,

3, Watford Villas, Battersea Park, S.W.

Science Master, Owens School, Islington. Science Lecturer, City of London College. A.R.C.S. (London); 1st Honours in Chemistry, South Kensington Exams.; Fellow of the Physical Society of London; Late National Scholar.

William A. Tilden. W. H. C. Jemmett.
W. Palmer Wynne. A. E. Dunstan.
Chapman Jones. *James C. Philip.*
M. O. Forster.

Davis, Henry Wilson,

18, Crescent Road, Kingston Hill, Surrey.

Analyst, Government Laboratory. First Class Certificate School of Mines, Theoretical and Practical Chemistry. Thirty years' experience in analytical work in Government Laboratory, London.

T. E. Thorpe. C. H. Burge.
H. J. Helm. J. Woodward.
Edwd. Jones. C. Proctor.

Ferris, Percy J.,

Heathfield, Seymour Grove, Old Trafford, Manchester.

Chemist in firm of Chemical Brokers, Liverpool. For 3 years student in Chemical Laboratories of the Owens College. For 1 year research student under Prof. W. H. Perkin.

H. B. Dixon. J. Campbell Brown.
W. H. Perkin, jun. Arthur Smithells.

J. Norman Collie.

Foll, Edgar William,

40, Sutton Street, Lambeth, S.E.

Brewer. Engaged at Lion Brewery, Belvedere Road, S.E. Have studied chemistry for a considerable period. During the past four years have been under the tuition of Matthew J. Cannon studying chemistry in relation to brewing. Obtained prize medal in brewing, 1899; silver medal honours, 1900, City and Guilds Examination. Have assisted Mr. Cannon in investigation work. Desire to join the Society to keep in touch with scientific progress.

Matthew J. Cannon. *C. A. Mitchell.*
M. Cannon. *Arthur R. Ling.*
J. Jackson. *Arthur Hartley.*

Francis, Francis E.,

8, Manilla Road, Clifton, Bristol.

Lecturer and Demonstrator in Chemistry, University College, Bristol. B.Sc. (Victoria); Ph.D. (Erlangen); A.I.C., 1892; Assistant Lecturer in Chemistry at Univ. Coll., Liverpool, 1895. Senior Lecturer and Demonstrator, Univ. Coll., Bristol, since 1896. Author of "Zur Kenntniss der *o*-Amidobenzylamine"; "The Dinitrosamines of Ethylenaniline and its Derivatives"; "The Separation of *N*- and *iso*-Heptane from American Petroleum"; "Action of Fuming Nitric Acid on Paraffins and other Hydrocarbons"; "Derivatives of Dibenzyl Ketone."

Sydney Young. Philip J. Worsley.
W. A. Shenstone. J. Campbell Brown.
W. Collingwood Williams.

Garle, John Longsdon,

136, Holland Road, Kensington, W.

Consulting Chemist. Student at University College, London.

Demonstrator at Pharmaceutical Society. Assistant to Charles J. Wilson, Esq. I am desirous of attending the meetings of the Society and obtaining its publications.

J. Norman Collie. Edward C. Cyril Baly.
William Ramsay. F. G. Donnan.
Charles J. Wilson.

Gow, Alexander,

38, Clarendon Street, Cambridge.

Student. Lecturer in Chemistry. Borough Road Training College, 1893–97. Chief Science Master, County High School, Isleworth. Isleworth, 1897–1900. B.Sc., London, 1893, in Chemistry. Studying Chemistry at Cambridge under Dr. Ruhemann.

S. Ruhemann. R. S. Morrell.
M. M. Pattison Muir. Hugh Ramage.
H. O. Jones.

Hallowell, Thomas Butterworth,

Ladyshawe House, New Mills, Derbyshire.

Analytical Chemist to Calico Printing Works, Birch Vale, Derbyshire. Having studied Chemistry at the Owens College, and been Assistant for five and a half years to A. W. Duncan, Esq., F.C.S., in the Analytical Laboratory of Messrs. J. Woolley, Ltd., Manufacturing Chemists, Manchester. Have held my present position for nearly two years.

Arthur W. Duncan. W. T. Lawrence.
Wm. A. Bone. J. F. Thorpe.
H. B. Dixon.

Hann, Archie Cecil Osborn,

54, Wood Vale, Forest Hill, S.E.

Teacher of Chemistry. For four years Student in the Chemical Dept., Goldsmiths' Technical Institute, New Cross. Now Assistant Lecturer in the same. Engaged on Research Work with Dr. Arthur Lapworth.

Arthur Lapworth. Stanley J. Peachey.
Alfred W. Harvey. Gerald T. Moody.
William J. Pope. Arthur H. Coote.

Harrison, Walter Ernest,

43, Mostyn Road, Handsworth, Staffs.

Science Master, Technical School, Handsworth. Associate of the Royal College of Science, London. Eight years Senior Science Master, Addey and Stanhope School, S.E. Now Science Master, Handsworth Technical School, Staffs.

Wm. Ping.	J. W. Shepherd.
J. H. Wolfenden.	*Chas. Wood.*
T. A. Cheetham.	*Chapman Jones.*
S. Whalley.	*James C. Philip.*
S. Parrish.	*Alex. W. Bain.*

Leader, George Herbert,

Sexey's School, Blackford, Wedmore, Somerset.

Senior Science Master at Sexey's Secondary and Technical School. A Student, during 1898, in the Chemical Laboratory of the Merchant Venturers' Technical College, Bristol. Chemical Laboratory of University College, Bristol, 1899—1900, and the Chemical Laboratory of University College, London, 1901. B.Sc. Lond. (with Honours in Chemistry and Zoology), 1901. Associate of University College, Bristol.

Sydney Young.	F. G. Donnan.
J. Wertheimer.	Edward C. Cyril Baly.
William Ramsay.	Morris W. Travers.

Lessner, Charles B.,

Fonda de Porto, Carril, Spain.

Metallurgical Chemist and Assayer. Studied Chemistry and Metallurgy at Battersea, Chelsea, and Woolwich Polytechnics, Northampton Institute, Birkbeck Institution, King's College, &c. Student Institution Mining and Metallurgy. Two years Assistant to Messrs. Holloway, Lake, and Currie. Assayer to the Kai Syndicate, Gold Coast Colony.

George T. Holloway.	Herbert S. Wallace.
Philip Schidrowitz.	Alec. A. Beadle.
C. J. Head.	John Wilson.

Moody, James Butler,

111, Manchester Road, Burnley, Lancs.

Head Brewer at Massey's Burnley Brewery Ltd., Burnley, Lancs.

Formerly student under Dr. Graham and Mr. Alfred C. Chapman, of London, and Dr. Miller, of Manchester.

Alex. K. Miller. Alfred Chapman.
John F. Rolfe. Tom Crossman.

Fred R. Stone.

Moore, Thomas Henry,

19, Sandmere Road, Clapham, S.W.

Chemist. Major Exam. of the Pharmaceutical Society.

W. Watson Will. *Frederick B. Power.*
Harold C. Sayer. *F. Filmer De Morgan.*
J. Bernard Coleman. *E. F. Harrison.*

O'Connor, Sinnott Valentine,

14, Selskar Street, Wexford.

Pharmaceutical and Analytical Chemist. A Licentiate of the Pharmaceutical Society by Examination.

Charles R. C. Tichborne. J. Armstedt Ray, jun.
Henry Boyers. *John Barclay.*

Thomas Tyrer.

Phillips, Percy Philip, Ph.D.

Haslemere, Morris Avenue, Manor Park, E.

Chemist. Certificate of the City and Guilds of London Institute in Applied Chemistry. Ph.D. Göttingen. Researches published: (1) "Amidoamidines of the Naphthalene Series," with Prof. Meldola (2) "Beiträge zur Kenntnis der D-d-Fenchenderivate und der Fenchocarbonsäure," with Professor Wallach.

Raphael Meldola. M. O. Forster.
G. T. Morgan. *James C. Philip.*

William Robertson.

Pollitt, George Paton, Ph.D.,

St. Silas's Road, Blackburn, Lancashire.

I have studied Chemistry at Owens College, Manchester, and at the Polytechnicum of Zurich under Professor Lunge. I have obtained the degree of Bachelor of Science, Hons. Chemistry of the Victoria University and that of Doctor of Philosophy of the University of Bâle, my Dissertation for which latter degree, "On the use of Oxide of Iron as Contact Substance in the manufacture of Sulphuric Anhydride from Sulphur Dioxide and Air," will shortly be published.

Harold B. Dixon. D. L. Chapman.
W. H. Perkin, jun. Wyndham R. Dunstan.
J. F. Thorpe. G. Lunge.

Powney, William H. F.,

67, Barretts Grove, Stoke Newington, London, N.

Analytical Chemist and Assayer; Chief Assistant to Geo. T. Holloway, Esq., Consulting Chemist and Metallurgist, of 57, Chancery Lane, London, W.C. Studied Chemistry for three years under Prof. Meldola, F.R.S., at Finsbury Technical College, Leonard Street, City Road, E.C. Have held present position for nearly six years. Qualified to teach Chemistry and Metallurgy under the Board of Education. Member of the Society of Public Analysts, and of the Society of Chemical Industry. Student-member of the Institution of Mining and Metallurgy.

George T. Holloway. Alec. A. Beadle.
Philip Schidrowitz. D. A. Louis.
Raphael Meldola.

Ralph, Stephen Jamieson,

22, Stanley Place, Eccleston Square, S.W.

Assistant Research Chemist. Certificated Student, Technical College, Finsbury. Research Assistant, Imperial Institute, Scientific Department.

Raphael Meldola. Ernest Goulding.
F. Southerden. Henry H. Robinson.
J. Vargas Eyre. Thomas A. Henry.
E. H. Miller.

Ralphs, Edwin,

Hongkong.

Senior Grade Master, Queen's College, Hongkong (Hongkong Civil Service). Student in Chemistry since 1885. First Class Advanced Certificates in Inorganic Chemistry (Theor. and Pract.), also First Advanced Certificates in Organic Chemistry (Theor. and Pract.), Science and Art Dept. Desire to keep in touch with Chemical Progress.

Charles A. Fogg. T. M. Nightingale.
A. L. Thornton. Walter Ratcliffe.
Harold Rostron. *Jno. L. Whiteside.*

Rây, Prafulla Chandra,

Calcutta.

D.Sc. (Edin.). Chemical Laboratory, Presidency College. Has

been for a long time Assistant to the Professor of Chemistry in the Presidency College, Calcutta. Is the author of several papers, principally upon the Nitrites of Mercury, which have appeared in the *Transactions*, *Zeit., anorg. Chem.*, *Annalen*, and Calcutta journals.

Alex. Crum Brown. James Walker.
J. Gibson. William Ramsay.

Edward Divers.

Roast, Harold James,

3, Manor Park Road, Harlesden, N.W.

Student of Chemistry three years. Engaged in Analytical work, and Assaying. Desire Membership of the Society as I wish to attend the meetings and to have the Society's Journal.

Isaac Sydney Scarf. John Grove Johnson.
Harold W. Harrie. Charles A. West.

H. Y. Loram.

Skertchly, William Pearson,

The Laboratory, 11, Billiter Square, E.C.

Analytical Chemist. Fellow of the Institute of Chemistry of Great Britain and Ireland, Member of the Society of Chemical Industry and of the Society of Public Analysts. Contributor of original papers to *The Analyst*. Eleven years Chief Assistant to Mr. Otto Hehner, F.I.C., F.C.S.

Otto Hehner. Bernard Dyer.
Alfred C. Chapman. Arthur R. Ling.

B. E. R. Newlands.

Stanger, William C. S.,

72, Belle Vue Road, Ipswich.

Schoolmaster, Higher Grade School, Ipswich. Student in Chemistry 1892—1895; Durham College of Science under Dr. Bedson, Prof. of Chemistry, A.Sc. (Durham) in Chemistry and Physics (1894). In sole charge of Chemical Dept., Ipswich Higher Grade School. Have now under instruction approx. 500 pupils in Chemistry per week.

P. Phillips Bedson. *S. Hoare Collins.*
F. C. Garrett. *E. J. Cox.*
Duncan T. Richards. *R. L. Taylor.*

W. J. Stainer.

Stewart, Hector,

479, Collins Street, Melbourne.

Mining Engineer and Metallurgical Chemist (M.C.E.). Master of Civil Engineering, Melb. Univ. Twelve months in charge of works for the treatment of gold ores, including chlorination, concentration, and assaying, Victoria. Four years assayer in charge of laboratory of the Lyell Tharsis M. Co., Tasmania, engaged on ore, rock, slag, and other analyses and assays. Memb. Austrn. Inst. of Mining Engineers.

H. W. Potts. R. Dubois.
Henry C. Jenkins. *A. W. Craig.*
J. Dennant.

Wells, John William,

Springburn, Blackburn.

Medical Practitioner. M.B., C.M. Edinburgh, 1887. D.P.H. (Victoria) 1901. Am engaged on experiments on the relation between chemical constitution of fats and their digestibility, and desire Chemical Society's publications.

Robert H. Pickard. Jas. F. Burnett.
Harold B. Dixon. William Lewins.
William Carter. *Arthur Clegg Bowdler.*
W. H. Duckworth. *Francis V. Darbishire.*

West, Joseph,

50, Poplar Grove, Fenton, Stoke-on-Trent.

Analytical Chemist. Analytical and Consulting Chemist to the Stafford Coal, Iron, and Chemical Works. Formerly of the Darwen and Mostyn Iron Works, Darwen. Lancashire and Cheshire 1st prize in Honours Chem. S.K. Formerly Student at Blackburn T. Schl. and Darwen T. Schl.

C. Gerland. George George.
G. W. Burman. *Harry W. Dixon.*
Geo. P. Rees.

Wheeler, Edward J.

Albany, State of New York.

Analytical and Consulting Chemist. Has taught chemistry since 1888 at different times at Williams College, at Union University, in departments of Medicine and Pharmacy. As Analyst in employ since 1891 of State of N.Y. Board of Health and Department of Agriculture, N.Y.

John A. Miller. Joseph F. Geisler.
Willis G. Tucker. E. G. Love.
J. H. Wainwright.

The following certificate was authorised by Council under Bye-law I. (3):

Purtan, Herbert,

London Chambers, Durban.

Public Analyst for Borough of Durban. Studied at Aberdeen University. Teacher of Chemistry at Seamen's Hospital, Greenwich. Assistant to R. H. Davies. F.I.C., &c., Apothecaries' Hall. Managing Director, Natal Chemical Co.

W. H. Pay. T. G. Macdonald.
J. S. Jamieson. *A. Pardy.*

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 25/6/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. No. 254.

Wednesday, June 18th, 1902. Professor EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

Messrs. Russell, Lattey, Ionides, Haas, and Heaton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Guy Dunstan Ricketts, Sir John Cass Technical Institute, E.C.
Edgar Stansfield, B.Sc., Technical College, Sunderland.
Thomas Edward Wallis, 78, Essex Road, Islington, N.

The PRESIDENT announced that the Council that afternoon had decided that the Ordinary Meetings of the Society for the ensuing session should be held, as far as possible, alternately, on Wednesdays at 5.30 p.m. and Thursdays at 8 p.m.

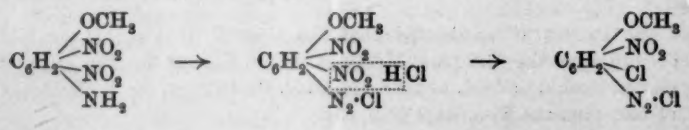
A Ballot for the Election of Fellows was held, and the following were subsequently declared duly elected:

James Handby Ball, B.Sc.
Edwin Thomas Holman Bucknell.
Bryce Chudleigh Burt, B.Sc.
Arthur Crozier Claudet.
William Thomas Clough.
Henry Wilson Davis.
Percy J. Ferris.
Edgar William Foll.
Francis E. Francis, B.Sc., Ph.D.
John Longsdon Garle.
Alexander Gow, B.Sc.
Thomas B. Hallowell.
Archie Cecil Osborn Hann.
Walter Ernest Harrison.
George Herbert Leader, B.Sc.
Charles B. Lessner.
James Butler Moody.
Thomas Henry Moore.
Sinnott Valentine O'Connor.
Percy Philip Phillips, Ph.D.
George Paton Pollitt, Ph.D.
William E. F. Powney.
Herbert Purtan.
Stephen Jamieson Ralph.
Edwin Ralphs.
Prafulla Chandra Rây, D.Sc.
Harold James Roast.
William Pearson Skertchly.
William C. S. Stanger.
Hector Stewart.
John William Wells.
Joseph West.
Edward J. Wheeler.

Of the following papers, those marked * were read:

***106. "Elimination of a nitro-group on diazotisation. Dinitro-*p*-anisidine." By R. Meldola and J. V. Eyre.**

Dinitro-*p*-anisidine, obtained by nitrating acet-*p*-anisidide and hydrolysing the acetyl derivative, was shown by the authors to have the constitution $C_6H_2NO_2{\cdot}NO_2{\cdot}NH_2{\cdot}OCH_3 = 2:3:4:1$. This compound, on diazotisation in acetic acid in presence of sulphuric or nitric acid, behaves normally and forms a dinitrodiazonium salt, which on heating with alcohol gives dinitroanisole, $C_6H_3{\cdot}NO_2{\cdot}NO_2{\cdot}OCH_3 = 2:3:1$, of m. p. 119°. The dinitrodiazonium salts combine with alkaline β-naphthol in the ordinary way to form the azo-compound, $CH_3O{\cdot}C_6H_2(NO_2)_2{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH\beta$. When diazotised in the presence of hydrochloric or acetic acid, one of the nitro-groups is eliminated as in the case of dinitro-*o*-anisidine (*Trans.*, 1900, **77**, 1172; *Proc.*, 1901, **17**, 131; *Trans.*, 1901, **79**, 1076). The authors showed that it is the 3-nitro-group, that is, the group which is *ortho* with respect to the diazonium group, which is thus eliminated. The product, when hydrochloric acid is used, contains chlorine in place of the 3-nitro-group, and is formed according to the scheme:



No diazoxide appears to be formed in this case, but the replacement of the nitro-group by chlorine takes place at once at the ordinary temperature. The chloronitrodiazonium salt, when boiled with alcohol, with or without the addition of alkali, gives chloronitroanisole, $C_6H_3 \cdot Cl \cdot NO_2 \cdot OCH_3 = 3:2:1$. The same diazonium salt, on combination with alkaline β-naphthol, gives the azo-compound, $CH_3O \cdot C_6H_2Cl \cdot NO_2 \cdot N_2 \cdot C_{10}H_6 \cdot OH\beta$. When diazotised in the presence of acetic acid alone, the NO_2 group is replaced by hydroxyl, and the diazonium salt combines with β-naphthol to form the hydroxyazo-compound, $CH_3O \cdot C_6H_2 \cdot NO_2 \cdot OH \cdot N_2 \cdot C_{10}H_6 \cdot OH\beta$. In this case, a diazoxide, $CH_3O \cdot C_6H_2 \cdot NO_2 \langle \overset{N_2}{O}$, may be formed as an intermediate product, but this has not yet been isolated.

The displacing of the nitro-group in the two dinitroanisidines now investigated tends to show that the elimination of this group follows the ortho-para law, and experiments for the purpose of testing this conclusion will be undertaken in due course.

***107. "Preliminary notice of some new derivatives of pinene and other terpenes." By W. A. Tilden and H. Burrows.**

Pinene nitrosochloride is remarkable as being the only known compound containing the elements of pinene from which that hydrocarbon may be regenerated. The addition of one molecule of hydrogen chloride to pinene gives the familiar monohydrochloride (artificial camphor, m. p. 128°), from which, by withdrawal of hydrogen chloride, camphene, and not pinene, results. The addition of two molecules of hydrogen chloride to pinene gives rise to dipentene dihydrochloride (m. p. 50°), from which, by removal of 2 molecules of hydrogen chloride, a mixture of liquid isomerides of pinene is obtained. On the other hand, when pinene combines with nitrosylchloride, a compound is formed which contains a nitroso-group. This is indicated by the fact that it is capable of reacting with aniline to yield a diazotised product, leaving a hydrocarbon which is apparently identical with pinene, though optically inactive (Wallach, *Ann.*, 1889, **252**, 132; 1890, **258**, 344).

The authors have repeated this experiment, and although the reaction is not so simple as they were led to infer from Wallach's account of it, they have verified the fact that the recovered hydrocarbon combines readily with nitrosylchloride, forming a nitrosochloride which melts at 110°, and from which a benzylnitrolamine melting at 125° was obtained. The corresponding compounds formed from ordinary dextro-pinene melt at 103° and 122—123° respectively (Wallach). The fact that this recovered pinene is optically inactive but not resolvable into two optical isomerides has not attracted the attention it

deserves. If optically inactive pinene really possesses the same constitution as active pinene, this would imply the existence in the molecule of two asymmetric carbon atoms similarly combined. The formulæ given by Wallach, Wagner, and other chemists are therefore inadequate to explain the facts.

In the hope of getting some new light on the problem, attempts have been made to produce new derivatives of the hydrocarbon by adding carbon in various forms to the unsaturated part of the molecule, with the idea of obtaining acids or other compounds of determinable constitution. Several methods have been tested in a preliminary way, but at present only one has met with success.

When pinene nitrosochloride is gently heated with an equivalent quantity of potassium cyanide in the presence of 90 per cent. alcohol, a compound having the composition of pinene nitrosocyanide is formed amounting to about 40 per cent. of the nitrosochloride employed. The viscous bye-products have not been completely examined. The cyanide is a crystalline compound which forms large prisms, of which the melting point is 171°. On analysis, the compound gave 14·47 per cent. of nitrogen, $C_{10}H_{16}NOCN$, requiring 14·58 per cent. It dissolves readily in alcohol, ether, acetic acid, and toluene, but very sparingly in light petroleum, and it is practically insoluble in water.

The constitution of this nitrosocyanide is at present an unsettled question. It is unaltered by boiling with 30 per cent. alcoholic potash for several hours. On the other hand, it is completely destroyed with formation of uncrystallisable products when heated with dilute sulphuric acid or with hydrochloric acid, either in alcoholic solution or in glacial acetic acid at 100°. It is therefore doubtful whether the compound is a nitrile. There are, however, other cases on record of nitriles which resist the action of alkalis, and the question is still under investigation.

By digesting the cyanide with alcoholic potash and methyl iodide, a methyl derivative is produced which is distinguished by the readiness with which it forms large, colourless, prismatic crystals. The melting point of this compound is 67°, and it contains 13·64 per cent. of nitrogen, $C_{10}H_{15}CH_3 \cdot NO \cdot CN$ requiring 13·60 per cent.

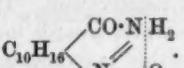
The action of reducing agents on the cyanide is rather remarkable. Three methods were successively employed, namely, (1) the action of sodium on a boiling solution of the cyanide in amyl alcohol, (2) the action of sodium on a boiling solution in ethyl alcohol, and (3) the action of zinc in the presence of alcohol and hydrochloric acid. In the reductions with sodium, some ammonia was evolved, and a cyanide was produced in considerable quantity, together with an almost quantitative yield of pinylamine.

The acid reducing agent produced practically no change, but when

zinc dust and an alkaline solution were employed ammonia was evolved, and on steam distillation, an oil of camphoraceous odour passed over.

A small quantity of a second crystalline, but not basic, compound, not yet investigated, was produced in both cases, and was extracted from the alkaline residue.

Pinene nitrosocyanide dissolves in concentrated sulphuric acid without coloration but with evolution of considerable heat. The solution, when diluted with water, yields the unchanged nitrosocyanide, but when the solution in sulphuric acid is digested at about 100° for an hour or two, the addition of water does not cause an immediate precipitate. On allowing the liquid to stand, a new compound is deposited in tufts of crystals, which, after recrystallisation from alcohol, appear in the form of well-defined plates which melt and decompose at about 220°. It is soluble in aqueous potash, and, somewhat strangely, also in hydrochloric acid. This compound contains 14·38 per cent. of nitrogen, which corresponds closely with the amount required either by a polymerised product, $(C_{10}H_{16}\cdot NO\cdot CN)_n$, or by the product which would result from the formation of the corresponding acid amide and the subsequent elimination of water, thus:



This is, however, a subject for further investigation.

Pinene nitrosocyanide, placed in contact with warm nitric acid (sp. gr. 1·4), liquefies but does not dissolve, while a small quantity of nitrous gas is evolved. In a few minutes, the reaction seems to be complete, effervescence ceases, and on pouring the whole into cold water, a solid is precipitated which crystallises readily from alcohol in colourless prisms. This compound is insoluble in aqueous alkali. It melts with decomposition at 105°. Analysis gave 16·30 per cent. of nitrogen. The formula of a mononitrocyanide, $C_{10}H_{16}\cdot NO_2\cdot CN$, requires 13·46, while that of a dinitrocyanide, $C_{10}H_{15}(NO_2)_2CN$, requires 16·60 per cent. of nitrogen. It is probable, therefore, that the nitroso-group is oxidised and nitration occurs at the same time.

An attempt to produce a nitrosocyanid from limonene nitrosochloride gave a liquid product which is awaiting further investigation. Terpinene nitrosate is also expected to yield corresponding products.

With regard to the hydrochlorides obtainable from pinene, the monohydrochloride (m. p. 128°) refused to react under any circumstances with either cyanide of potassium or of silver. An alcoholic solution of dipentene dihydrochloride digested with potassium

cyanide in the cold for 14 days gave the liquid monohydrochloride, $C_{10}H_{16}$,HCl, and the latter, by continuing the action of the cyanide at about 120°, gave very pure terpinene, which was identified by its boiling point (181°) and by the production of the characteristic crystalline nitrosate.

*108. "The colour changes exhibited by the chlorides of cobalt and some other metals from the standpoint of the theory of electro-affinity." By F. G. Donnan and H. Bassett, jun.

The colour changes exhibited by aqueous and alcoholic solutions of the chlorides of cobalt, copper, and ferric iron on variation of temperature or dilution, or on the addition of various chlorides, such as those of hydrogen, calcium, magnesium, zinc, mercury, are shown to be largely due to the formation or dissociation of complex anions containing a metallic atom in association with chlorine. Evidence was brought forward to show that the dehydration theory is inadequate to explain the observed phenomena. Experiments on the motion of boundaries between different liquid layers on the passage of an electric current point to the existence of complex negative ions. Thus, in the case of cobalt chloride, the blue solutions travel towards the anode, the red solutions towards the cathode. Further experiments on the combination between cobalt and other chlorides in aqueous and alcoholic solutions admit of explanation on the above hypothesis.

*109. "The stereochemical formulæ of benzene." By J. E. Marsh.

The author discussed the objections to the stereocentric formulæ of benzene brought forward by Graebe (*Ber.*, 1902, **35**, 526), and pointed out that according to the latter, rings identical in structure, which their properties do not admit of, would be assigned to benzene and naphthalene. The author considers that all the eight stereocentric formulæ are possible for benzene and its derivatives; that orthophthalic acid would have the *trans*-centric form, in which case it could form an anhydride, though the meta-acid could not, since the hexahydro-ortho-acid alone forms an anhydride in the *trans*-form. Thus, proximity of groups alone would not account for the formation of anhydrides, nor of carbonates and methylene ethers of dihydric phenols. Further, the absence of optically active compounds is accounted for if we regard the Kekulé formula as a labile form of the *cis*-centric, for the Kekulé model can close in in two ways to form *cis*-centric formulæ, one being the optical image of the other.

With regard to substitution, those compounds which yield meta-derivatives contain an oxidisable group, whilst those which yield ortho-

and para-derivatives contain a reducible group. In the former case, the repulsion of hydrogen leads to the *trans*-centric form with production of meta-derivatives. In the latter case, the attraction of hydrogen to the group leads to *cis*-centric hydrogen in the ortho- and para-positions. Bamberger's dicentric formula for naphthalene was also criticised, as it appears stereochemically impossible and is not in accord with the constitution of allied hydrocarbons.

***110. "An accurate method of determining the compressibility of vapours." By B. D. Steele, D.Sc.**

In the course of an investigation with Prof. Ramsay, it became necessary to determine, with a high degree of accuracy, the compressibility of certain vapours at low pressures. The apparatus employed consists of a combination of volume apparatus and pressure gauge, so constructed as to be capable of being contained together in a glass jacket which can be maintained at a constant temperature. The pressure is measured by setting two surfaces of mercury to carefully ground glass points the difference in level between which is known. The volume is obtained by weighing the mercury entering or leaving the apparatus.

Experiments with the vapours of benzene and ether have been made in the apparatus, and curves obtained showing the variation of PV with P for pressures varying from 40 to 200 mm.

***111. "A new type of substituted nitrogen chlorides." By F. D. Chattaway.**

No substituted nitrogen chlorides known up to the present have three negative groups attached to the nitrogen. All contain at least one hydrocarbon residue.

Such a series of compounds of the type $\begin{matrix}R\\R'\end{matrix}\!>\!N\cdot Cl$, where R and R' are acyl groups, is yielded by the diacyl amides. These, when treated with hypochlorous acid or, under certain conditions, with chlorine have their imino-hydrogen replaced by chlorine, thus:

$$\begin{matrix}R\\R'\end{matrix}\!>\!N\cdot H + HOCl \rightleftharpoons \begin{matrix}R\\R'\end{matrix}\!>\!N\!\begin{matrix}Cl\\H\\OH\end{matrix} \rightleftharpoons \begin{matrix}R\\R'\end{matrix}\!>\!N\cdot Cl + H_2O.$$

The diacyl nitrogen chlorides are colourless, well-crystallised compounds which show the typical behaviour of substances having halogen attached to nitrogen.

Dibenzoyl Nitrogen Chloride, $\begin{matrix}C_6H_5\cdot CO\\C_6H_5\cdot CO\end{matrix}\!>\!N\cdot Cl$.—In order to obtain

this compound, dibenzamide, prepared by the action of fuming sulphuric acid and phosphorus pentoxide on benzonitrile, was dissolved in acetic acid. To the solution, an excess of a strong solution of bleaching powder was added. Chlorine was vigorously evolved and a yellow oil separated. Chloroform was added and the whole well shaken for a few minutes. The chloroform solution was then run off, washed with water, and finally with a dilute solution of potassium bicarbonate, dried over fused calcium chloride, and the solvent evaporated at a low temperature in a rapid current of dry air. The nitrogen chloride crystallised out as a white solid (m. p. 89°), readily soluble in chloroform and in benzene, but sparingly in petroleum. It crystallises from a mixture of chloroform and petroleum (b. p. 60—80°) in colourless, six-sided prisms with domed ends. It was analysed in the usual way, by adding an excess of hydriodic acid to a weighed quantity dissolved in chloroform, and estimating the liberated iodine by a standard solution of sodium thiosulphate:

0·2446 liberated I = 18·7 c.c. *N*/10 I. Cl as :N·Cl = 13·55.
$C_{14}H_{10}O_2$:N·Cl requires Cl as :N·Cl = 13·65 per cent.

When heated with water or dilute acids it is hydrolysed, hypochlorous acid being liberated and dibenzamide re-formed, the latter undergoing further hydrolysis to benzoic acid and benzamide, and finally, if the heating be prolonged, to benzoic acid and ammonia.

Di-p-toluyl Nitrogen Chloride, $\begin{matrix}CH_3\cdot C_6H_4\cdot CO\\CH_3\cdot C_6H_4\cdot CO\end{matrix}\!\!>\!N\cdot Cl$.—This was prepared from di-*p*-toluylamide by the method previously described. It closely resembles the dibenzoyl derivative in properties and in solubility. It crystallises in long, colourless, six-sided prisms with domed ends (m. p. 129°).

0·2121 liberated I = 14·8 c.c. *N*/10 I. Cl as :N·Cl = 12·37.
$C_{16}H_{14}O_2$:N·Cl requires Cl as :N·Cl = 12·32 per cent.

The author desires to reserve the further investigation of these and similar compounds.

***112. "The preparation of pure chlorine and its behaviour towards hydrogen." By J. W. Mellor and E. J. Russell.**

A quantity of carefully dried and purified silver chloride was placed in a V-shaped tube of the hardest Jena glass, in which were also inserted, as electrodes, stout carbon rods specially prepared for the electrolysis of fused salts. An air-tight joint having been made, the salt was fused and a current of 2·8 amperes passed through. Chlorine was evolved in a steady stream. Foreign gases and mois-

ture were removed by occasional reversal of the current and repeated exhaustion with an automatic Sprengel pump.

The silver tree was destroyed by raising the temperature and increasing the current to 5 amperes. The tree then either melted or was shattered; electrolysis was discontinued until the former temperature was restored; when started again, it was found to proceed in a normal manner.

Hydrogen was prepared by the action of steam on sodium and was absorbed by palladium. The whole apparatus was then exhausted, the palladium heated, and hydrogen evolved.

The gases were sealed up in the inner and outer bulbs respectively of the condensers now largely used with Soxhlet extractors. Each bulb contained a quantity of carefully purified phosphorus pentoxide, the inner bulb containing also a small piece of glass rod. After drying for some months in the dark, the vessels were shaken to break the inner bulb and the gases mixed by diffusion. Only condensers which had approximately equal capacities for the inner and outer bulbs were used; hydrogen was put in at the same pressure as the chlorine, so that the volumes of the two gases were nearly equal.

A small electric spark passed through a mixture so obtained caused an explosion, and combination was found to have been practically complete. Apparently drying does not affect the action of the spark.

Mixtures of moist hydrogen and chlorine in similar bulbs were found to explode at about 260°. One of the bulbs containing the purified mixture was therefore heated to 270° for some minutes, but no explosion took place. On opening the bulb, it was found that there had been practically no combination. Another bulb was heated for 10 minutes to 450°. Still no explosion occurred, but about 80 per cent. of the mixture had combined. Some of the phosphorus pentoxide had volatilised, and as it was found impossible to heat the gases without also heating the pentoxide, it is still uncertain whether this slow combination is a direct action or a surface action. Another bulb was exposed to bright sunshine at Wye for 3 days, but no explosion took place; and only about 30 per cent. of the hydrogen and chlorine had combined.

***113. "Derivatives of dibenzoylmesitylene." By W. H. Mills and T. H. Easterfield.**

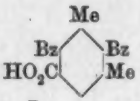
The authors described a method of preparing dibenzoylmesitylene by which it may be obtained in quantity, and methods for the production and isolation of the five acids which result by the successive oxidation of its methyl groups, namely, *asym.*dibenzoylmesitylenic acid, m. p. 174°, *sym.*dibenzoylmesitylenic acid, m. p. 222°, *asym.*dibenzoyluvitic

acid, m. p. 211°, *sym.*dibenzoyluvitic acid, m. p. 262°, and dibenzoyltrimesic acid, m. p. 250°.

A mixture of these, of which *asym.*dibenzoylmesitylenic acid is by far the largest constituent, is obtained by boiling the ketone with dilute nitric acid the boiling point of which has been raised by the addition of large quantities of potassium and sodium nitrates.

The two dibenzoyluvitic acids are most conveniently prepared by treating the easily obtainable *asym.*dibenzoylmesitylenic acid with one equivalent of potassium permanganate in alkaline solution. If double this amount of potassium permanganate be used, dibenzoyltrimesic acid is obtained.

The constitution of these acids readily follows from the following facts:



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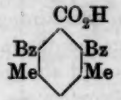

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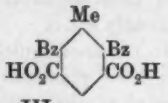

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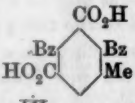

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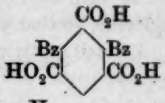
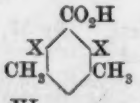


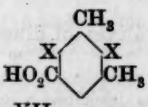
V.

The dibenzoylmesitylenic acid of melting point 174°, oxidised with potassium permanganate, yields a mixture of *both* dibenzoyluvitic acids. It must therefore be the asymmetrical acid of formula I. The dibenzoylmesitylenic acid of melting point 222°, similarly treated, yields only *one* dibenzoyluvitic acid melting at 211°. Hence, it must be represented by formula II and the dibenzoyluvitic acid resulting from it by IV. The dibenzoyluvitic acid melting at 262° must therefore be represented by III, and for dibenzoyltrimesic acid, only one formula is possible, namely, V.

In working with these acids, the fact was discovered (also noticed by Graebe, *Ber.*, 1900, **33**, 2026) that diortho-substituted acids do not obey V. Meyer's esterification rule when the ortho-substituents are benzoyl groups:



VI.



VII.

whereas it follows from V. Meyer's work that the esterification constant of an acid of formula VI would in general be indefinitely smaller at the ordinary temperature than that of an acid of formula VII, in

the case where X is a benzoyl group it is smaller only in the ratio of approximately 0·65 to 1·0.

114. "The molecular condition of borax in solution." By H. S. Shelton.

Borax (Shields, *Phil. Mag.*, 1893, **35**, 365) is slightly hydrolysed into sodium hydroxide and boracic acid. Experiments on the diminution of conductivity on the addition of further quantities of boracic acid show an increase of this hydrolysis when further diluted with water, and also with increase of temperature. In *N*/10 solution, the hydrolysis was estimated by Shields to be 0·5 per cent. at 25°, and the experiments of the author with *N*/200 solution showed 4 per cent. at 25° and 6 per cent. at 50°. Kahlenberg and Schreiner (*Zeit. Phys. Chem.*, 1896, **20**, 547) concluded from freezing point determinations that six chemical individuals are present in a dilute solution of borax.

These chemical individuals seem to be $2H_3BO_3$, $^{+}2NaBO_2^{-}$, as shown by the following equation:

$$Na_2B_4O_7Aq + 3H_2O = 2NaAq, 2BO_2Aq + 2H_3BO_3.$$

The author has confirmed this by a number of direct experiments, amongst which the most important is the precipitation of $AgBO_2$, and determination of the boracic acid remaining in the solution.

115. "On the union of hydrogen and chlorine. Part V." By J. W. Mellor, D.Sc.

There is no experimental evidence to show that chlorine gas under the influence of light undergoes any change capable of appreciably affecting the chemical activity of that element towards hydrogen. Part of the energy absorbed by moist chlorine from sunlight is dissipated as heat. This causes the Budde effect. Under the influence of light, chlorine sets up and maintains in a state of equilibrium a reversible reaction with water vapour, possibly $2H_2O + 2Cl_2 \rightleftarrows 4HCl + O_2$. Dry chlorine does not exhibit the Budde effect. The rise in temperature of imperfectly dried chlorine when exposed to sunlight appears to be due to some chemical reaction between the moisture and the chlorine gas. A layer of moist chlorine just thick enough to screen a bulb of mixed hydrogen and chlorine gases from chemical action is not sufficient to prevent chemical action if the chlorine is dried by means of purified phosphorus pentoxide. The actinic energy continuously absorbed from sunlight by moist chlorine is dissipated in at least three ways: (1) in maintaining the above chemical reaction

(2) by conversion into heat during molecular impacts; (3) as external non-actinic radiations from the molecules moving in their free path between molecular collisions.

116. "On the union of hydrogen and chlorine. Part VI." By J. W. Mellor, D.Sc.

If the reaction between hydrogen and chlorine in the presence of moisture is assumed to take place with the formation of an intermediate compound, the period of induction is a direct consequence of the law of mass action. Since neither chlorine monoxide nor hydrogen hypochlorite abbreviate the period of induction, neither of these substances can take part as intermediate compounds in the reaction between hydrogen and chlorine. Since chlorine acquires no appreciable chemical activity by exposure to sunlight, the presence of hydrogen as well as of moisture determines the greater chemical activity of an induced mixture of hydrogen and chlorine gases. If an intermediate compound takes part in the reaction between hydrogen and chlorine in the presence of moisture, the most probable "compound" satisfying the required conditions contains xCl_2,yH_2O,zH_2, where x, y, z, are positive integers. The explanation offered by the two dependent reactions involved in the equation,

$$\begin{matrix}Cl\\Cl\end{matrix} + \begin{matrix}H\\H\end{matrix}\!\!>\!O + \begin{matrix}H\\H\end{matrix} = \begin{matrix}ClH\\ClH\end{matrix} + O\!<\!\begin{matrix}H\\H'\end{matrix},$$

remains to be studied.

117. "On some hydroxy-pyrone derivatives." By T. Tickle and J. N. Collie, F.R.S.

During some work on the constitution of meconic acid, the authors found that it was necessary to prepare certain hydroxypyrone derivatives in order to compare their properties (especially their colour reactions with ferric chloride) with those of meconic acid.

Dimethylpyrone, when treated with hydrogen peroxide in presence of a ferrous salt, yields hydroxydimethylpyrone, $C_7H_8O_2 + H_2O_2 = C_7H_8O_3 + H_2O$. This substance crystallises from water in colourless needles; it can be sublimed without decomposition and melts at 162·5°. With ferric chloride, it gives a deep violet-blue colour. Its monacetyl derivative melts at 98° and does not colour an aqueous solution of ferric chloride.

Meconic acid, when treated in the same manner with hydrogen peroxide, gives carbon dioxide and hydroxycomenic acid, $C_7H_4O_7 + H_2O_2 = C_6H_4O_6 + CO_2 + H_2O$. Hydroxycomenic acid seems to be a dibasic acid; it gives an intense violet with ferric chloride, melts at

275°, and crystallises from water in long, fine needles. It seems probable that this is the same acid as that first obtained by Reibstein (*J. pr. Chem.*, 1881, [ii], **24**, 286) by the action of barium hydroxide on bromocomenic acid. He, however, gives no melting point for the acid, but only for the ethyl ester, 204°, and for the diacetoxyl derivative, 75°. The authors find that these derivatives prepared from this acid melt at 207·5° and 75° respectively.

All attempts to prepare either meconic acid or hydroxycomenic acid by oxidation of chelidonic acid were unsuccessful.

118. "The absorption spectra of phloroglucinol and some of its derivatives." By W. N. Hartley, D.Sc., F.R.S., J. J. Dobbie, D.Sc., M.A., and A. Lauder, B.Sc.

Phloroglucinol reacts with some reagents as a phenol, with others as a ketone. It is impossible, therefore, from its chemical behaviour to decide whether its oxygen atoms are present in hydroxyl groups or in direct union with carbon. The trimethyl derivative of phloroglucinol (m. p. 52°) is regarded as a true ester, since its methoxyl groups are split off by heating with hydrogen iodide. The absorption spectra of this substance and of phloroglucinol were found to be almost identical. From this it follows that if the structure of the ester has been correctly established, phloroglucinol also must have the enolic structure (*Trans.*, 1899, **76**, 640; 1900, **77**, 839). Aqueous and alcoholic solutions of phloroglucinol show both general and selective absorption. A layer 50 mm. thick of a solution containing 1 milligram-mol. in 20 c.c. water, absorbs all rays beyond λ 3009, whilst a layer 5 mm. thick absorbs all rays beyond λ 2802. The absorption-band is not strongly marked; it appears first in a layer 3 mm. thick of the solution containing 1 milligram-mol. in 100 c.c. water, and nearly dies out in a layer 2 mm. thick, although its position is still distinctly traceable by the weakness of the spectra in solutions of greater dilution. The resemblance between the spectra of phloroglucinol and the trimethyl derivative is so close that phloroglucinol cannot consist of a mixture of the enolic and ketonic forms.

The specimens of phloroglucinol examined were prepared from five different sources, namely, kino, maclurin, resorcinol, phenol (by fusion with sodium hydroxide), and phloroglucinoltricarboxylic ester. The specimens from these various sources had the same melting point. The melting point is greatly influenced by the rate of heating, varying between 210° and 217°. The absorption curves of all the specimens agree perfectly. The authors conclude from the identity of the spectra that the structure of phloroglucinol, no matter from what source it is obtained or by what method it is prepared, is always the same.

The spectra of pyrogallol were also re-examined, and the curve was found to resemble very closely that of phloroglucinol, thus confirming the conclusion that the latter substance has the enolic structure.

119. "Solubility of mannitol, picric acid, and anthracene." By A. Findlay.

Determinations of the solubility of mannitol in water, of picric acid in water and in benzene, and of anthracene in benzene, have been made at several temperatures between 25° and 60°.

It has already been shown by the author (*Proc. Roy. Soc.*, 1902, **69**, 471) that if the solubility curve of one substance is known, that of another substance can be calculated from two, or better, three, determinations of the solubility of the second substance at different temperatures. The formula used for this purpose is one analogous to that employed by Ramsay and Young for the calculation of vapour pressures, and has the form $T_1/T_1' = T_2/T_2' + c(t' - t)$, where T_1/T_1' and T_2/T_2' denote the absolute temperatures at which the two substances have the same solubility, c is a constant, and t' and t are the temperatures at which one of the substances has the solubility corresponding to the absolute temperatures T_1 and T_2 or T_1' and T_2'. This formula has been employed in the present case for calculating the solubilities of the above substances between 0° and 25°, and between 60° and 100° (in the case of anthracene and picric acid, in benzene up to the boiling point of the latter).

120. "Menthyl formylphenylacetate." By J. B. Cohen and S. H. C. Briggs.

A short time ago, the authors commenced a similar investigation to that of Lapworth and Hann (this vol., p. 144) with the object of studying tautomeric changes by means of optically active substances, in the course of which they prepared menthyl formylphenylacetate described by Lapworth and Hann. As the authors do not intend, under the circumstances, to pursue this line of inquiry, they desire to record their observations, which, though they confirm on the whole the results given in the paper referred to, show some slight differences. Menthyl formylphenylacetate was prepared as follows. Sodium was allowed to act on a mixture of menthyl acetate and ethyl formate dissolved in dry ether. In this reaction, an interchange occurs to some extent between the menthyl and ethyl groups so that some menthyl formate, and some ethyl formylphenylacetate are produced. The product was poured into water, the ethereal layer removed, and the aqueous portion acidified and shaken out with ether. The ether was

evaporated in a vacuum, and crystals of menthyl formylphenylacetate separated on standing. The menthyl ester thus obtained was in the form of large, well-formed, tetragonal crystals consisting of four-sided prisms terminated by pyramids; purified by recrystallisation from chloroform, it melted at 82—84° (L. and H. give 82—83°). The specific rotation of a freshly prepared chloroform solution containing about 3 grams of substance in 100 c.c. is $[\alpha]_D^{18°} = -72{\cdot}6°$ (L. and H. give $-74{\cdot}6°$). In an alcoholic solution containing 2 grams in 100 c.c., the specific rotation was $[\alpha]_D^{18°} = -63{\cdot}9°$ (L. and H. give $-64{\cdot}9°$). The addition of sodium ethylate did not affect the rotation. The following were the effects of an alcoholic solution of ferric chloride on the substance when dissolved in various solvents. A faint violet coloration was produced in methyl and ethyl alcohol, ether, and light petroleum. No coloration was produced at first in benzene, chloroform, or ethyl acetate but slowly developed. Menthyl phenylacetate, obtained in the preparation of the formylphenylacetate, is a colourless and odourless liquid which boils at 216° (39 mm.).

***121. "Transformation of diacetanilide into aceto-*p*-amino-acetophenone." By F. D. Chattaway.**

A large number of derivatives of primary aromatic amines in which various atoms or groups are attached to the nitrogen readily undergo intramolecular transformation and form isomerides in which the atom or group is attached to the nucleus in the para- or ortho-position. The best known examples of such changes are those in which a halogen atom, a nitro-group, a sulphonic group, or a hydroxyl group passes on to the ring. So far, however, the commonest substituting group in amines, the acetyl group, has not been observed to wander. The author described experiments in which this group passed into the ring in the normal manner. The substance studied was diacetanilide, which underwent transformation into aceto-*p*-amino-acetophenone.

122. "Nitrogen chlorides and bromides derived from ortho-substituted anilides." By F. D. Chattaway and J. M. Wadmore.

Nitrogen halogen derivatives of orthochlorobenzanilide and orthobromobenzanilide, which have not hitherto been described, are easily obtained by treating the corresponding anilides with an excess of hypochlorous or hypobromous acid, the actions, as in other similar cases, being reversible. The nitrogen chlorides and bromides so obtained show all the typical nitrogen halogen group reactions and readily undergo transformation into the isomeric 2:4-disubstituted anilides.

The following compounds have been prepared:

Benzoyl-o-chlorophenyl nitrogen chloride, $C_6H_4Cl{\cdot}NCl{\cdot}COC_6H_5$, colourless, six-sided plates, m. p. 94°. *Benzoyl-o-chlorophenyl nitrogen bromide*, $C_6H_4Cl{\cdot}NBr{\cdot}COC_6H_5$, short prisms of a deep yellow colour, m. p. 110°. *o-Bromobenzanilide*, $C_6H_4Br{\cdot}NH{\cdot}COC_6H_5$, colourless, rectangular plates, m. p. 116°. *Benzoyl-o-bromophenyl nitrogen chloride*, $C_6H_4Br{\cdot}NCl{\cdot}COC_6H_5$, colourless, transparent prisms, m. p. 85°. *Benzoyl-o-bromophenyl nitrogen bromide*, $C_6H_4Br{\cdot}NBr{\cdot}COC_6H_5$, yellow, six-sided, rhombic prisms, m. p. 99°. *Acetyl-o-chlorophenyl nitrogen bromide*, $C_6H_4Cl{\cdot}NBr{\cdot}COCH_3$, pale yellow, four-sided prisms, m. p. 152°. *Acetyl-o-bromophenyl nitrogen chloride*, $C_6H_4Br{\cdot}NCl{\cdot}COCH_3$, colourless, four-sided prisms, m. p. 86°.

123. "Substituted nitrogen chlorides containing the azo-group." By F. D. Chattaway.

In order to determine the effect of an azo-group on the properties and direction of transformation of nitrogen chlorides, a number of such compounds have been prepared from aminoazobenzene. Aminoazobenzene yields well crystallised acetyl, propionyl, and benzoyl derivatives, which react with hypochlorous acid very readily and form nitrogen chlorides possessing all the characteristic properties of the nitrogen halogen group. This adds another to the many reasons for regarding aminoazo-compounds as primary amino-derivatives.

The following compounds have been prepared:

p-Acetylchloroaminoazobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NCl{\cdot}COCH_3$, orange-red plates, m. p. 113·5°. *Propionyl-p-aminoazobenzene*, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}COC_2H_5$, large, orange-red plates, m. p. 170°. *p-Propionylchloroaminoazobenzene*, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NCl{\cdot}COC_2H_5$, red prisms, m. p. 57°. *Benzoyl-p-aminoazobenzene*, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}COC_6H_5$, reddish-orange plates, m. p. 211°. *p-Benzoylchloroaminoazobenzene*, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NCl{\cdot}COC_6H_5$, red-brown, glistening, flattened prisms, m. p. 144°.

124. "The action of chlorine and bromine on nitroaminobenzenes. Part I. *s*-Trisubstituted chloronitroaminobenzenes." By K. J. P. Orton.

In the course of an investigation of the conditions under which the nitroamines derived from *s*-trisubstituted anilines (this vol., p. 111) are transformed into substances containing the nitro-group in the benzene nucleus, the action of chlorine and bromine on these substances was studied.

When chlorine is passed into an aqueous solution of the sodium salt of a nitroamine, or when dilute aqueous bleaching powder is slowly added to a solution of the nitroamine in acetic acid, the chloronitro-

amine is formed; thus 1-nitroamino-*s*-trichlorobenzene yields 1-*chloronitroamino-s-trichlorobenzene*, $C_6H_2Cl_3\cdot NCl\cdot NO_2$.

As the sodium (and other) salts of the nitroamines may probably be represented by the formula $R\cdot N{:}NO\cdot ONa$, and, if so, would be the salts of a substituted "iminonitronic acid" (compare Bamberger, *Ber.*, 1902, **35**, 54), the author suggested that the reaction of chlorine with the sodium salt might be represented thus:

$$R\cdot N{:}NO\cdot O^{-}Na^{+} + Cl_2 \longrightarrow R\cdot \underset{Cl}{N}\cdot \underset{Cl}{NO}\cdot O^{-}Na^{+} \longrightarrow$$

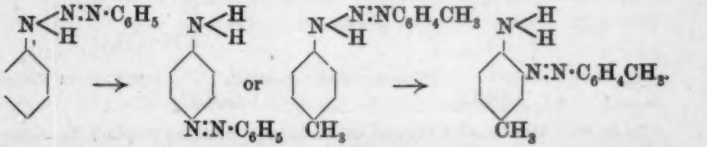
$$R\cdot NCl\cdot NO_2 + Cl^{-}Na^{+}.$$

All these chloronitroamines are very unstable, and are reconverted by all reagents into the nitroamines. The following compounds, all of which crystallise in lustrous, colourless prisms, have been prepared: 1-*Chloronitroamino-s-trichlorobenzene*, m. p. 53—54°; 1-*chloronitroamino-s-tribromobenzene*, m. p. 61°; 1-*chloronitroamino*-4-*chloro*-2 : 6-*dibromobenzene*, m. p. 56°; 1-*chloronitroamino*-2 : 3 : 4 : 6-*tetrabromobenzene*, m. p. 61—62°; 2-*chloronitroamino*-3 : 5-*dibromotoluene*, m. p. 60°; 4-*chloronitroamino*-3 : 5-*dibromotoluene*, m. p. 50—51°.

By the action of bromine on aqueous solutions of the sodium salts of the nitroamines, the bromonitroamino-derivatives are formed, but have not been obtained free from the nitroamine.

125. "The transformation of diazoamido- into aminoazo-compounds and of hydrazobenzene into benzidine." By F. D. Chattaway.

The transformation of diazoamido- into the isomeric aminoazo-derivatives is similar in nature to the other well-known transformations in which atoms or groups of atoms pass from the nitrogen of an amino-group attached to a benzene nucleus into the para- or ortho-position in the ring, thus:



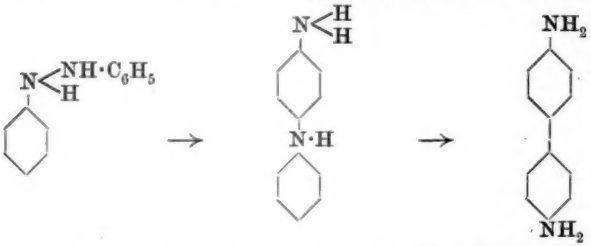
As is usual in these intramolecular changes, the para-position is taken up by preference, the ortho-position to a less extent, or exclusively when the para-position is already occupied.

This analogy is somewhat obscured by the ordinary method of representing the transformations,

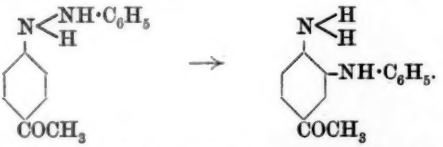
where the NH group appears to leave the chain and pass into the ring.

The formation of the various azo-derivatives which are obtained by heating diazoamido-compounds with aromatic amines and their hydrochlorides, is thus rendered intelligible without assuming the formation of intermediate nitrogen halogen compounds (Goldschmidt and Bardach, *Ber.*, 1892, 25, 1376). It is only necessary to assume the existence of a mobile hydrogen atom and double linkage in the diazoamido-compounds, and to admit that the diazo-group can undergo transference from the nitrogen atom of one amine to that of another, present in large excess, exactly as a chlorine or bromine atom does. Much that is known of similar isomeric changes points to the conclusion that transference from nitrogen to the ring can only take place when the nitrogen is exerting its higher valency. This may explain the advantage, in these transformations, of the hydrochloride of the base.

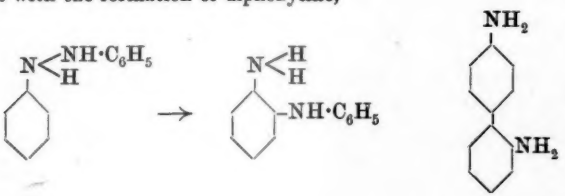
The isomeric change of hydrazobenzene into benzidene is also brought into line with other analogous transformations if similarly formulated:



It is seen to consist of two stages, of which the first only can take place if the para-position is already occupied, the semidine and other similar transformations resulting:



As is well known, the related ortho-change also takes place to some extent with the formation of diphenyline,



in all probability, the ortho-change also takes place to a relatively very small extent in the second stage with the production of diorthoaminodiphenyl, though the latter is produced in such small quantity that it has hitherto escaped detection.

126. "Tribromophenolbromide." By E. W. Lewis.

A re-examination of this substance has shown that the melting point usually attributed to it (118°) is much too low, and that it may be raised to 148—149° by recrystallising the compound from ethyl acetate; moreover, whilst, as usually stated, the substance of low melting point gives off bromine on heating at about 125°, the purified material begins to lose bromine before melting at about 145°.

The crystals of tribromophenolbromide belong to the orthorhombic system, the axial ratios being $a : b : c = 0{\cdot}7945 : 1 : 1{\cdot}5921$.

ADDITIONS TO THE LIBRARY.

I. Donations.

Mann, Harold H. Studies in the chemistry and physiology of the tea leaf. Part I. The enzymes of the tea leaf. Pp. 13. 1901. From the Author.

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LIBRARY.

The Library will be closed for stock-taking during the first fortnight of August. Fellows are particularly requested to return all Library books in their possession not later than July 26th.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY

Issued 14/11/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. No. 255.

The following are abstracts of papers received during the vacation, and published, or passed for publication, in the *Transactions*:

127. "On the solvent properties of mixed liquids in relation to the chemical characters and solvent properties of their components." By H. M. Dawson.

The solvent power of mixtures of liquids in its relationship to that of the components has been investigated under conditions such that complicating secondary effects of electrolytic dissociation, high concentration of the solutions, and interaction of the component liquids are avoided.

Measurements of the solubility of iodine were obtained by determining the ratio of distribution between water as standard substance on the one hand, and mixtures of organic solvents on the other. A method of determining this partition ratio is described in which an aqueous solution of potassium iodide is employed instead of pure water. If the iodine concentration in the aqueous solution remains the same in all experiments, the conditions of experimentation correspond almost exactly with the determination of the solubility of a gas in different liquids, the pressure of the gas being kept constant. The organic solvents chosen were such as would not be expected to have any action on each other, or on the dissolved iodine. In

these circumstances, it is found that in the majority of cases the solvent power of the mixture is less than the sum of the solvent powers of the components; sometimes, however, it is equal to, or greater than, the sum of the solvent powers of the components. No case of a maximum or minimum solvent power, such as that observed with alcohol-water mixtures in regard to hydrogen, oxygen, carbon monoxide, and carbon dioxide has been found.

128. "Notes on luteolin and apigenin." By A. G. Perkin.

Kiliani and Mayer (*Ber.*, 1901, **34**, 3577) have recently asserted that the author's tetrabenzoyl-luteolin (*Trans.*, 1896, **69**, 209) is in reality a tribenzoyl derivative. A re-examination of the original preparation shows that the statement of Kiliani and Mayer is incorrect, and that the substance is without doubt tetrabenzoyl-luteolin. Further experiments with reference to the tinctorial properties of apigenin and chrysin confirm the previous results of the author (*Trans.*, 1897, **71**, 806).

129. "Note on a simple form of Landsberger's apparatus." By E. B. Ludlam.

A description is given of an apparatus which has proved most satisfactory to work with. The tube in which the rise of temperature is measured is graduated and placed in the neck of the flask containing the boiling solvent, the vapour of which enters it from below by means of a simple valve which serves the double purpose of regulating and breaking up the stream of vapour, and also of preventing the solution from running back into an intermediate tube, placed between the increcometer and the flask, when the latter is cooled.

The graduated tube is also provided with an annular trough which serves as a trap and catches the liquid condensed in the upper part of the tube, conveying it to the condenser, thus making the increase of volume in the tube much slower than it otherwise would be.

130. "The action of substituting agents on benzeneazo-β-naphthol." By J. T. Hewitt and S. J. M. Auld.

Bromine added to benzeneazo-β-naphthol suspended in glacial acetic acid furnishes *p*-bromobenzeneazo-β-naphthol, a result also obtained by Margary (*Gazzetta*, 1883, **13**, 438), who assigned to the substance the melting point 160—161°, but which the authors, like Bamberger, find to be 172—173°. In presence of sodium acetate, such a high temperature is necessary before the bromine will attack the azo-compound that

the results obtained lead to no definite conclusion as to the structure of benzeneazo-β-naphthol.

Nitric acid in presence of concentrated sulphuric acid nitrates the azonaphthol in the benzene nucleus (para-position), dilute nitric acid attacks benzeneazo-β-naphthol on warming, giving 1 : 6-dinitro-β-naphthol as the chief product, and *p*-nitrobenzeneazo-β-naphthol in smaller amount.

With strong acids, benzeneazo-β-naphthol behaves as a quinone-hydrazone; with dilute acids (nitric) or weak acids (acetic) its reactions are more those of an azonaphthol.

131. "The condensation of dimethylaminobenzaldehyde with β-naphthol. By J. T. Hewitt, A. J. Turner, B.Sc., and S. W. Bradley.

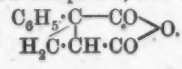
When hydrochloric acid is added to a solution of dimethylamino-benzaldehyde and β-naphthol in cold glacial acetic acid, crystals of the composition $HCl,(CH_3)_2N\cdot C_6H_4\cdot CH(C_{10}H_6OH)_2$ are deposited; these darken at about 150° and melt at 215° with decomposition. If, however, a mineral acid be added to a hot glacial acetic acid solution of the aldehyde and β-naphthol, a salt of the corresponding anhydride is produced.

Attempts at oxidation were without result; even bromine does not yield an oxonium salt, but gives the bromide of a bromo-substitution product, $C_{29}H_{29}BrON,HBr$ (m. p. 196°, uncorr.).

132. "The action of ethyl chlorofumarate on monoalkylmalonic esters." By S. Ruhemann.

The author finds that, in the presence of sodium ethoxide, ethyl chlorofumarate reacts with the mono-alkyl derivatives of ethyl malonate to yield homologues of ethyl carboxyaconitate according to the equation:

$$R\cdot CNa(CO_2Et)_2 + CO_2Et\cdot CCl{:}CH\cdot CO_2Et = R\cdot C(CO_2Et)_2\cdot C(CO_2Et){:}CH\cdot CO_2Et + NaCl.$$

The quantity of the unsaturated ester which is produced is small, and decreases as the radicle in the substituted malonic ester increases. Of several homologues prepared, the author has studied especially ethyl phenylcarboxyaconitate, $C_6H_5\cdot C(CO_2Et)_2\cdot C(CO_2Et){:}CH\cdot CO_2Et$, and finds that, on hydrolysis, it loses two molecules of water, and yields a compound, $C_{11}H_8O_3$, which is the anhydride of a dicarboxylic acid. This anhydride is not an unsaturated compound, but a derivative of trimethylene having the formula  . On re-

duction with sodium amalgam, this compound yields *s*-phenylmethylsuccinic acid, $C_6H_5 \cdot CH(CO_2H) \cdot CH(CH_3) \cdot CO_2H$ (m. p. 193°), which is identical with the acid described by Zelinsky and Buchstab (*Ber.*, 1891, **24**, 1876).

133. "Di-*sec.*-octyl tartrate and di-*sec.*-octyl dibenzoyl tartrate." By J. McCrae.

Di-*sec.*-octyl tartrate was prepared from ethyl octyl tartrate and octyl alcohol by the hydrochloric acid method. It is an oil which boils at 225° (20 mm.) and has $[\alpha]_D^{18°} = 7{\cdot}06°$. The dibenzoyl derivative was prepared by acting on the ester with excess of benzoyl chloride and was purified by precipitation with water from an alcoholic solution. It is an oil with $[\alpha]_D^{22°} = -43{\cdot}94°$. The rotations of these two compounds are compared with those of other tartaric esters.

134. "Glycogen from yeast." By A. Harden and W. J. Young.

The glycogen of yeast was extracted by grinding the yeast with sand, pouring the mass into boiling water, and purifying the glycogen by a combination of the methods of Clautriau and Pflüger. Expressed yeast juice was employed. The glycogen, free from ash and nitrogen, was compared with glycogen extracted by Pflüger's method from rabbit liver and from oysters.

All three samples, dried at 100° in a vacuum over phosphorus pentoxide, were found to have the composition $C_6H_{10}O_5$ and not $6C_6H_{10}O_5 + H_2O$. Glycogen dried at 100° in air always retained a certain amount of water.

The specific rotations were found to be, rabbit glycogen $[\alpha]_D^{15°} = +191{\cdot}1°$; oyster glycogen $[\alpha]_D^{15°} = +191{\cdot}2°$; yeast glycogen $[\alpha]_D^{16{\cdot}8°} = +198{\cdot}3°$.

In view of the low concentrations of the solutions rendered necessary by their opalescence, this difference cannot be considered as characteristic.

The glycogen from yeast appears to be identical with animal glycogen in composition and optical activity. Slight differences appear to exist in its behaviour towards dilute acids, in the reaction with iodine, and in the opalescence of the aqueous solutions, but these are also exhibited by glycogens derived from various animal sources.

135. "The action of acetylene on the acetates of mercury." By E. Burkard, Ph.D., and M. W. Travers, D.Sc.

The authors have investigated the compounds produced by the action of acetylene on mercurous and mercuric acetates respectively, which were briefly described by the late Dr. R. T. Plimpton (*Proc.*, 1892, **8**, 109).

The mercurous compound, which is explosive, has the formula C_2Hg_2,H_2O, and resembles the already well-known acetylides of silver, copper, and mercury.

The mercuric compound appears to be a definite basic acetylide of the formula $3C_2Hg,2HgO,2H_2O$ or $3C_2Hg,2Hg(OH)_2$; it is non-explosive.

Both compounds yield acetylene when treated with acids, and a mixture of di-iodoacetylene and tetraiodoethylene when treated with iodine. Hence it appears that the oxygen and hydrogen in the compounds are connected with the mercury rather than with the carbon.

136. "The decomposition of water vapour by the electric spark." By D. L. Chapman and F. A. Lidbury.

The experiments described show that when electric sparks are passed through water vapour the decomposition which takes place is considerable. The products of decomposition are partly separated from one another and take up different positions in the tube. The separation which occurs cannot be entirely accounted for by electrolysis for the following reasons:

(1) Hydrogen collects at both electrodes and oxygen in the middle of the spark gap.

(2) The hydrogen which collects at the cathode is very largely in excess of that required by Faraday's law.

137. "The chlorination of the dichlorotoluenes in presence of the aluminium-mercury couple. The constitution of the trichlorotoluenes." By J. B. Cohen and H. D. Dakin.

The six dichlorotoluenes were chlorinated, using the aluminium-mercury couple as carrier. In order to identify the products formed, the six trichlorotoluenes were prepared synthetically, together with their nitro- and dinitro-derivatives and the trichlorobenzoic acids which they yield on oxidation. The results show that the six dichlorotoluenes, on chlorination, give five out of the six possible trichlorotoluenes.

138. "The constitution of the nitro- and dinitro-derivatives of the dichlorotoluenes." By J. B. Cohen and H. D. Dakin.

The authors have determined the constitution of the nitro- and dinitro-derivatives of the six dichlorotoluenes which they had previously prepared (*Trans.*, 1901, 79, 1111). They find that in the case of the mono-substitution derivatives, the chlorine atoms possess a greater influence than the methyl group in determining the position of the entering nitro-group, whilst in the case of the dinitro-compounds the position of the first entering nitro-group appears to be of primary importance in determining the position to be occupied by the second nitro-group, for in all the six dichlorodinitrotoluenes the nitro-groups are in the *meta*-position to one another.

139. "Iodonium compounds of the type IR′R″R‴, and the configuration of the iodine atom." By H. Peters.

Further investigation of the phenyl-*p*-tolyliodonium bromocamphorsulphonate described in a previous note (*Proc.*, 1900, **16**, 62) has confirmed the conclusion that it cannot be resolved into salts of enantiomorphously related bases, from which the inference may be drawn that the three iodine valencies are situated in one plane, two of them being symmetrically situated with respect to the third.

In the preparation of phenyl-*p*-tolyliodonium iodide from iodoso-*p*-toluene and iodoxybenzene, small quantities of *di-p-tolyliodonium iodide* are formed owing to secondary reactions; similarly, the crude phenyl-*p*-tolyliodonium iodide, prepared from iodosobenzene and iodoxy-*p*-toluene, contains small quantities of diphenyliodonium iodide. The formation of these subsidiary products is not due to extramolecular change of the radicles of the phenyl-*p*-tolyl salt, and it is shown that the latter is really the salt of a mixed iodonium base.

Phenyl-p-tolyliodonium nitrate, $Ph(C_6H_4\cdot Me)I\cdot NO_3$, crystallises in prisms melting at 117°. The *chloride*, $Ph(C_6H_4\cdot Me)I\cdot Cl$, crystallises in needles and melts at about 193°.

Di-p-tolyliodonium iodide, $(C_6H_4Me)_2I\cdot I$, forms well-defined, octahedral crystals and decomposes at 143—153°.

Di-p-tolyliodonium bromocamphorsulphonate, $(C_6H_4Me)_2I\cdot C_{10}H_{14}BrO_4S$, crystallises in needles melting at 185—186°; it is sometimes obtained in hydrated dodecahedra, very like the crystals of the corresponding salt of the mixed base.

Diphenyliodonium bromocamphorsulphonate, $(C_6H_5)_2I\cdot C_{10}H_{14}BrO_4S$, forms hydrated dodecahedra, the anhydrous salt melting at 165—168°.

140. "Influence of substitution on the formation of diazoamines and aminoazo-compounds. Part II." By G. T. Morgan, D.Sc.

Mixed diazoamines containing a naphthalene nucleus are readily obtained from the diazotised *o*- and *m*-nitranilines and 1-chloro-β-naphthylamine. The properties and reactions of several are described in detail in the paper.

141. "Observations on the phenomena and products of the decomposition of normal cupric acetate when heated." By A. Angel and A. V. Harcourt.

The authors give a summary of the numerous researches on this subject. One phenomenon which had not been noted previously is the formation of a bright coating of copper in the test-tube in which the salt $[Cu(C_2H_3O_2)_2,H_2O]$ is heated. As this salt does not fuse this must be due to a gaseous compound of copper, proved by the authors to be cuprous acetate, which volatilises at about 200° and forms, especially when sublimed in hydrogen, feathery, white crystals.

The salt was heated generally in a tube in an oil-bath, and kept nearly vacuous by a Sprengel pump and the gases collected. These were found to consist wholly of the oxides of carbon in approximately the ratio $4CO_2 : CO$. The liquid products consisted of water and acetic acid with a trace of acetone. The fixed residue is of a paler or deeper red-brown colour, and consists of metallic copper mixed with a bulky black substance the composition of which may be represented by the formula $C_{11}H_4O_4$.

142. "The resolution of β-hydroxybutyric acid into its optically active components." By A. McKenzie.

In a preliminary note (*Proc.*, 1901, **17**, 213), the author mentioned that he had obtained *l*-β-hydroxybutyric acid from the inactive acid by aid of the quinine salt.

The *d*-acid has since been isolated by means of the strychnine salt the solvent being ethyl acetate. It was found that for it $[\alpha]_D^{16°} = +24{\cdot}3°$ ($c = 2{\cdot}226$).

Change of concentration has little influence on the value for the specific rotation of the acid (Magnus-Levy) and the salts are active in the same sign as that of the acid but to a less degree. In these respects, β-hydroxybutyric acid differs from most other aliphatic oxy-acids.

When the *l*-acid is heated at 100°, it is partly converted into an anhydride.

When the inactive potassium and sodium salts were respectively injected subcutaneously into dogs, the author found from examination of the urine (1) that acetoacetic acid and acetone were present, (2) that a small portion of the β-hydroxybutyrates was unattacked, and (3) that this product was lævorotatory.

Partial resolution of the acid was also obtained by esterification with *l*-menthol and *l*-borneol.

143. "The rate of decomposition of diazo-compounds. Part I. Diazo-compounds of the benzene series." By J. C. Cain and F. Nicoll.

The decomposition of an aqueous solution of a diazo-salt is in most cases a simple monomolecular one, conforming to the expression $C = \frac{1}{t} \log \frac{A}{A-x}$.

The authors have measured the rate of decomposition of diazo-salts from various bases and find that at temperatures between 20° and 60° the diazo-salts from aniline and the toluidines conform to the above law, thus confirming some results of Hantzsch at 25° (*Ber.*, 1900, **33**, 2517), but being quite opposed to the work of Hausser and Muller at 40° and 64° (*Bull. Soc. chim.*, 1892, [iii], **7**, 721; 1893, **9**, 353).

The authors maintain that the assumption by the latter chemists of a specific "retarding action" of the phenol formed cannot be upheld.

A table of constants of the diazo-salts from eight amines shows the very great stability of the diazo-salts from substances containing an acid group (NO_2 or SO_3H). The diazo-salt from *p*-amidoacetanilide follows the law only in acetic acid solution, as in presence of mineral acid the acetyl group is saponified.

Of the tetrazo-salts of the diamines, only that from dichlorobenzidine follows the law. The others give in the case of the tetrazo-salts from benzidine and tolidine diminishing, and in the case of that from dianisidine, increasing, values for C, pointing to the probability of the formation of an intermediate substance containing still a diazo-group.

144. "Studies upon the action of sodamide and acetyl substituted sodamides upon organic esters." By A. W. Titherley, D.Sc., Ph.D.

Sodamide appears to form addition compounds containing the grouping $-C\begin{matrix}OR\\ -NH_2\\ ONa\end{matrix}$ when allowed to act on esters in benzene solution if the temperature is kept low. On warming, further action at once

takes place, which varies according to the nature of the ester. With esters of benzoic and other purely aromatic acids, an alcohol splits off and a substituted sodamide results.

With esters of fatty and phenyl aliphatic acids, the final result of the reaction is a condensation effected on very similar lines to those brought about by sodium ethoxide, and probably by a similar mechanism.

Phenyl benzoate behaves quite differently from the ethyl ester in giving sodium dibenzamide and phenoxide, and the reaction proceeds with great readiness. Ethyl oxalate gives an intermediate product which with water yields sodium oxamate.

The action of sodamide with ketones is very different in the aliphatic series when condensations are brought about from that in the pure aromatic, where there is no action. Acetone with sodamide gives, in presence of benzene after a vigorous reaction, a jelly consisting essentially of the sodium derivatives of the enolic forms of mesityl oxide, phorone, and isophorone.

The interaction of acyl-substituted sodamides and esters depends largely on the nature of both these substances, which, if aliphatic, induce various complex changes. In the pure aromatic series, a simple definite change occurs which conforms approximately to the reversible system,

$$R{\cdot}CO{\cdot}NHNa + R{\cdot}CO_2R' \rightleftharpoons (R{\cdot}CO)_2N{\cdot}Na + R'{\cdot}OH,$$

but in all probability the mechanism of the reverse reaction is more complex.

The reaction is capable of modification in numerous ways, and the acyl-substituted sodamide may be prepared from the amide and alcoholic sodium ethoxide, or (best) from sodamide. A very good yield of dibenzamide is obtainable from sodium benzamide and ethyl benzoate.

Thursday, November 6th, 1902. Professor McLeod, F.R.S., Vice-President, in the Chair.

The Chairman referred to the great loss which the Society had sustained since its last meeting by the deaths of Sir Frederick Abel and Dr. J. H. Gladstone, two of its Past Presidents, who had been for more than fifty years Fellows of the Society.

Messrs. Garle, Hann, Pollitt, Gill, Moore, and Parkes were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

John Frederick Alder, 13, Priestwood Mansions, Highgate, N.
Alfred Edward Beanes, Moatlands, Paddock Wood.
Herbert Blair, No. 3, General Hospital, Kroonstad.
John A. H. Brincker, B.A., M.B., 7, St. Mary's Terrace, Paddington, W.
Vernon Seymour Bryant, B.A., Camborne, Cornwall.
Thomas Burnell Carmichael, Parton, Whitehaven.
Charles Cockle, Peter Symonds School, Winchester.
James Justinian Drought, Johannesberg.
Walter Henry Edwards, The Grammar School, Wellingborough.
Wilfrid Russell Grimwade, B.Sc., Melbourne.
Edward Gumersall, Atbara, Sidcup.
David V. Hollingworth, Aldred House, Crescent, Salford.
Alfred Holt, jun., B.A., Crofton, Aigburth, Liverpool.
Clements F. V. Jackson, A.Inst.C.E., Brisbane.
John Petty Leather, 17, Carlton Road, Burnley.
Frank A. Lidbury, M.Sc., Owens College, Manchester.
Ernest Liotard, 2, Rue de France, Nice.
Thomas Stratford Logan, 52, Kirkgate, Leeds.
Douglas A. MacCallum, Shawlands, Glasgow.
William Mann, B.Sc., Fonnereau Villa, Dartford.
John Marsh, 29, High Street, Maidstone.
Joseph William Mellor, D.Sc., Owens College, Manchester.
John Price Millington, B.A., Christ's College, Cambridge.
John Phelps, B.A., Trinity College, Oxford.
George A. P. Ross, M.B., B.Ch., 20, Westhall Gardens, Edinburgh.
John William Sampson, Helpringham, Heckington.
Duncan Simpson, 10, Brynmill Crescent, Swansea.
Robert Walter Sindall, 80, Manor Road, Brockley, S.E.
John Seabury Smythe, B.Sc., Ph.D., 143, Smithdown Lane, Liverpool.
Walter F. Sutherst, Ph.D., Agricultural College, Holmes Chapel.
George Sutherland Thomson, Government Offices, Adelaide.
Henry Letheby Tidy, B.A., New College, Oxford.
William Carter White, 113, Gower Street, W.C.
Lyndon Wilson, 66, Castle Gate, Newark-on-Trent.

Of the following papers, those marked * were read:

***145. "The specific heats of gases." By H. Crompton.**

It was shown that the molecular heat of any gas at the absolute temperature T may be calculated with the help of a formula of the type $A + BT$. In this formula A has the same value for all gases and depends on changes in the movements of the molecules of the gas as

a whole. B is proportional to $V \times \log n$, where V is the volume of the molecule and n is the number of atoms in the molecule. BT depends on interatomic changes taking place within the molecule. If for V the molecular volume at the normal boiling point of the liquid Mv_b is taken, the molecular heat at constant pressure $C_p = 4{\cdot}935 + 0{\cdot}000245 Mv_b T \log n$ (or if common logarithms are used the coefficient is 0·000564). The molecular heats calculated from this formula are shown to be in fair agreement with those observed. The ratio k of the two specific heats can also be calculated with the aid of this formula.

Discussion.

Dr. Travers remarked that it would be interesting to know how closely the formula would reproduce the values of the specific heats of the commoner gases, which had been determined with great accuracy and over a considerable range of temperature by Regnault, Witkowski, and others. The agreement between the observed and calculated values in the cases cited by the author was, however, remarkable.

Dr. Philip pointed out that the values of C_p given by the two formulæ (Le Chatelier's and that of the author) would, owing to the difference in the numerical constants chosen, be more divergent the lower the temperature. On this account, a study of the applicability of the proposed formula at low temperatures would be specially interesting.

Mr. Crompton, in reply, admitted that at low temperatures the results given by the formula did not agree with the observed so well as those obtained at higher temperatures. In explanation of this, he pointed out that the formula was only supposed to hold for an ideal gas, no account being taken of the effect on the specific heat of possible attractions between the molecules. If such attractions existed, they would have a greater influence on the specific heat at low temperatures, and this the nearer the gas was to its point of liquefaction, than under ordinary conditions. No doubt a term should be introduced to allow for the effect of molecular attractions, but at present he was unable to make any suggestion with reference to the character of this correction.

*146. "The action of nitric acid on bromophenolic compounds." By W. Robertson.

The action of nitric acid on bromophenols and their derivatives was studied in order to determine the conditions under which the bromine atom is replaceable by nitroxyl. It has been found that if the hydrogen of the hydroxyl group be replaced by either the methyl or

acetyl radicle, no displacement of bromine by the nitro-group occurs when these substances are acted on by nitric acid under similar conditions. The bromohydroxybenzoic acids and their methoxy- and acetoxy-derivatives were also prepared, and it was found that with regard to them the same rule applied.

The following compounds were described: 2 : 6-dibromo-4-acetyl aminophenol, needles, m. p. 185—186° (Hölz, *J. pr. Chem.*, 1886, [ii], **32**, 68, gives 173—174°; Friedländer and Stange, *Ber.*, 1893, **26**, 2262, 185°); *2-nitro-6-bromo-4-acetylaminophenol*, yellow needles melting at 230°; *2-nitro-6-bromo-4-benzoylaminophenol*, yellow needles, m. p. 247°; 2 : 3 : 6-*tribromo-4-acetylaminophenol*, white needles, m. p. 224° with decomposition; 2 : 6-dibromo-4-anisidine, white, glistening leaflets, m. p. 66° (Stadel, *Annalen*, 1883, **217**, 70, does not give melting point), and its *acetyl* and *benzoyl* derivatives which crystallise in needles melting at 206° and 180° respectively; *acetyl-3 : 5-dibromosalicylic acid*, m. p. 156°; *acetyl-5-bromosalicylic acid*, m. p. 168°; *acetyl-3 : 5-dibromo-p-oxybenzoic acid*, m. p. 207°; *ethyl ester* of *3 : 5-dibromo-p-oxybenzoic acid*, needles, m. p. 99°; *acetyl-3-bromo-p-oxybenzoic acid*, m. p. 155°; a *dibromo-m-oxybenzoic acid*, m. p. 202°; *2-bromo-4 : 6-dinitro-3-oxybenzoic acid*, a yellow substance, m. p. 217—218°.

Discussion.

Mr. W. A. Davis pointed out that although Mr. Robertson had been unable to isolate intermediate products of nitration in the case of the bromo-phenols he had dealt with, such substances had been obtained by Armstrong and Rossiter in the form of nitrobromo-keto-naphthalenes (*Proc.*, 1891, **7**, 89). He himself had for several years been working with this class of compounds and had found that their stability depends largely on the proportion of bromine which they contain. Thus, whilst the nitro-keto-compound of β-naphthol is so unstable that it cannot be isolated, and the keto-derivatives of bromo-, dibromo-, and tribromo-β-naphthol are stable only at low temperatures, those formed from the tetrabromo- and pentabromo-naphthols can usually be kept for several days in the dry state without undergoing change. Moreover, whilst the lower brominated keto-compounds are readily reduced to the corresponding bromonitro-naphthols by sodium sulphite, those derived from the tetrabromo-β-naphthols are reducible only by concentrated hydriodic acid.

*147. "3 : 5-Dichloro-*o*-xylene and 3 : 5-dichloro-*o*-phthalic acid." By A. W. Crossley and H. R. Le Sueur.

The high boiling fraction of the liquid obtained by the action of phosphorus pentachloride on dimethyldihydroresorcin, consists of

3 : 5-*dichloro-o-xylene*, $C_6(CH_3)_2H_2Cl_2$, which may also be produced by the prolonged heating of dichlorodimethyldihydrobenzene with phosphorus pentachloride. It is a faintly yellow, highly refractive liquid, which boils at 129° (23 mm.) or at 226° (atmospheric pressure), and on cooling solidifies to a mass of flaky needles melting at 3—4°.

On oxidation with nitric acid, it is converted into 3 : 5-*dichloro-o-phthalic acid*, $C_6H_2Cl_2(CO_2H)_2$, which crystallises in hair-like needles melting at 164° with previous contraction and sublimation. The *anhydride* (m. p. 89°) and several other derivatives have been prepared.

***148. "The combination of carbon monoxide with chlorine under the influence of light." By G. Dyson and A. Harden.**

Following the method previously described (*Proc.*, 1894, 10, 165), the authors have found :

(1) That when a mixture of carbon monoxide and chlorine, dried by being passed through sulphuric acid, is exposed to light, a well-marked period of photochemical induction occurs.

(2) The induction lapses slowly when the exposed gas is placed in the dark.

(3) The sensitiveness of this mixture to light is greatly diminished by admixture of air, but is not much affected by the presence of carbonyl chloride, hydrogen chloride, excess of carbon monoxide, vapour of carbon tetrachloride, and small amounts of water vapour.

DISCUSSION.

Professor TILDEN said one point which Dr. Harden had omitted to mention was the extent to which the gases had been deprived of moisture. He would be glad to hear by what method they had been dried, and whether the authors had observed that the composition of the glass or the condition of the surface in contact with the gases produced any influence on the rate of their combination.

Dr. HARDEN replied that the gases were dried by being bubbled through strong sulphuric acid. They had not made any experiments specially with reference to the composition of the glass or the condition of its surface.

***149. "The constituents of commercial chrysarobin." By H. A. D. Jowett, D.Sc., and C. E. Potter, B.Sc.**

Araroba, or Goa powder, and commercial chrysarobin, the substance obtained from the former by extraction with solvents as chloroform, have been investigated by Attfield, by Liebermann and Seidler, and by Hesse with varying results. The latter chemist found that crude

chrysarobin contained no chrysophanic acid, but was a mixture of two parts of chrysarobin, $C_{15}H_{12}O_3$, and one of its methyl ether. He regarded chrysarobin as the anthranole of chrysophanic acid. The authors have examined commercial chrysarobin and find that it contains the following substances, but no chrysophanic acid.

Chrysarobin, $C_{15}H_{12}O_3$, is the anthranole of chrysophanic acid and identical with chrysophanohydroanthrone obtained by the reduction of chrysophanic acid. It melts at 204°. When acetylated with acetic anhydride alone, a mixture of diacetylchrysarobin (m. p. 193°) and triacetylchrysarobin (m. p. 238°) is obtained, but if sodium acetate and acetic anhydride are used, the triacetyl compound is alone produced.

Methyl ether of *dichrysarobin*, $C_{31}H_{26}O_7$, melts at 160°. It yields a soluble pentacetyl compound, m. p. 135°, identical with Hesse's hexacetyldichrysarobin.

Dichrysarobin, $C_{30}H_{24}O_7$, does not melt below 250°, but blackens and chars gradually. On acetylation, hexacetyldichrysarobin (m. p. 179—181°) is obtained. The formula assigned to this constituent is proved by analysis.

A *substance*, $C_{17}H_{14}O_4$, m. p. 181°, which yields an acetyl compound, m. p. 215—216°.

The two latter substances are contained in crude chrysarobin in only small amount, the greater portion consisting of the two first-named substances. Methylchrysarobin was not found to be a constituent of crude chrysarobin. Both chrysarobin and dichrysarobin yield chrysophanic acid on oxidation, and β-methylanthracene by distillation with zinc dust.

Crude chrysophanic acid as obtained from rhubarb contains pure chrysophanic acid, m. p. 190° (acetyl compound, m. p. 206°), and the methyl ether of dichrysarobin, and not the methyl ether of chrysophanic acid as previously stated by Hesse.

***150. "The constituents of an essential oil of rue." By F. B. Power and F. H. Lees.**

In order to prepare some methyl nonylketone, the authors obtained a quantity of oil of rue labelled *Ol. Rutae., Ang.*, from an English distiller and found subsequently, on inquiry, that it was not distilled from the native-grown herb. From their results, taken in conjunction with those of Thoms (*Ber. deut. pharm. Ges.*, 1901, **10**, 3) and von Soden and Hexle (*Pharm. Zeit.*, 1901, **46**, 277 and 1026), the authors regard it as most probably of Algerian origin.

The oil was light brown in colour. d 15·5°/16° = 0·8405, α_D = − 3°48′ for a 100 mm. tube. It was completely soluble in two parts

of 70 per cent. alcohol. The following constituents were identified: (1) methyl *n*-heptylketone, b. p. 194·5—195·5° at 763 mm., d 14°/16° = 0·8296 (semicarbazone, m. p. 119—120°); (2) methyl *n*-nonylketone, b. p. 231·5—232·5°, d 20·5°/16° = 0·8263 (semicarbazone, m. p. 122°); (3) methyl *n*-heptylcarbinol, b. p. 198—200°, d 19°/16° = 0·8273, α_D = −3°44′ in a 50 mm. tube; *acetate*, b. p. 213—215°, d 20·5°/16° = 0·8605, α_D = −3°3′ in a 50 mm. tube (oxidation of alcohol to the corresponding ketone, b. p. 195—199°, semicarbazone, m. p. 118—119°); (4) methyl *n*-nonylcarbinol, b. p. 231—233°, α_D = −1°18′ in a 25 mm. tube (oxidation to corresponding ketone, oxime, m. p. 46—47°); (5) a blue oil of high but not constant boiling point; (6) acetic acid; (7) a basic substance having the odour of quinoline; (8) a mixture of free fatty acids; (9) methyl salicylate; (10) an ester of valerianic acid, apparently ethyl valerianate; (11) pinene (nitrosochloride, nitrolpiperidide, m. p. 119—120°); (12) *l*-limonene (tetrabromide, m. p. 103°); (13) cineol (compound with tetraiodopyrrol, m. p. 114—115°, and hydrobromide, m. p. 55—56°).

The relative proportions in which the above-mentioned substances were found to exist in the oil are approximately as follows: the two ketones constitute 80 per cent., and were present in about equal amounts. The two alcohols represent about 10 per cent., the methyl *n*-heptylcarbinol preponderating; they were present partly in the free state and partly as acetic esters. The terpenes, together with cineol, amount to about 1 per cent., and the blue oil to about 0·5 per cent. From the non-ketonic portion of the oil, a small amount of an undistillable, viscous substance, probably a decomposition product, was separated.

Since the substances associated with the ketones and alcohols are present in such small amount, and the limonene is the more rarely occurring *l*-form, the authors conclude that all these substances are natural constituents of the oil.

*151. "Methyl β-methylhexyl ketone." By F. H. Lees.

Ethyl sec.*-hexylacetoacetate*, $CH_3 \cdot CO \cdot CH(C_6H_{13}) \cdot CO_2Et$, was prepared by the condensation in alcohol at 100° of ethyl sodioacetoacetate with *sec.*-hexyl iodide; it is a colourless oil which boils at 130—132° (17 mm.), and at 243—245° under atmospheric pressure.

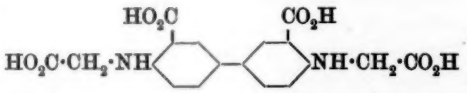
Methyl β-methylhexyl ketone, $CH_3 \cdot CO \cdot CH_2 \cdot CH(CH_3) \cdot (CH_2)_3 \cdot CH_3$, was prepared by the hydrolysis of ethyl *sec.*-hexylacetoacetate with 30 per cent. aqueous potassium hydroxide. It is a colourless oil with a pleasant, fruity odour, boiling at 184° (769 mm.), and having the density d 15°/16° = 0·8319. Its *semicarbazone* forms needles and melts at 75°; its *oxime* is a colourless oil.

152. "Di-indigotin." By J. Moir, M.A., D.Sc.

The author's object in the following experiments was to prepare the diphenyl analogue of indigotin, in order to ascertain what influence the doubling of the molecule would have on the colour, since this exercises a marked influence in the case of the benzidine dyes as compared with ordinary azo-dyes derived from aniline. Although successful in preparing the new substance, the yield was so poor and its properties so troublesome to investigate that only a meagre description of it is possible.

The method consisted in applying the synthesis of indigo employed by F. Baeyer & Co. to benzidinedicarboxylic acid instead of to anthranilic acid.

4 : 4′-Benzidine-3 : 3′-dicarboxylic acid was prepared from *o*-nitrobenzoic acid by reduction with sodium hydroxide and aluminium powder until the solution, which was at first dark red, became paler by the conversion of azo- to hydrazo-acid ; it was then precipitated with excess of acetic acid, and the hydrazo-acid thus obtained boiled with strong hydrochloric acid to convert it into the benzidine derivative, which was obtained on dilution as an almost insoluble powder, coloured pale green by some oxidation product which could not be removed. It was dissolved in the smallest possible quantity of potassium carbonate solution and mixed with excess of neutral potassium monochloracetate solution. On boiling the mixture for some hours, a small quantity of a crystalline precipitate was obtained, which was filtered off and dried. It melted above 300° and is probably bisphenylglycine-*o*-carboxylic acid,

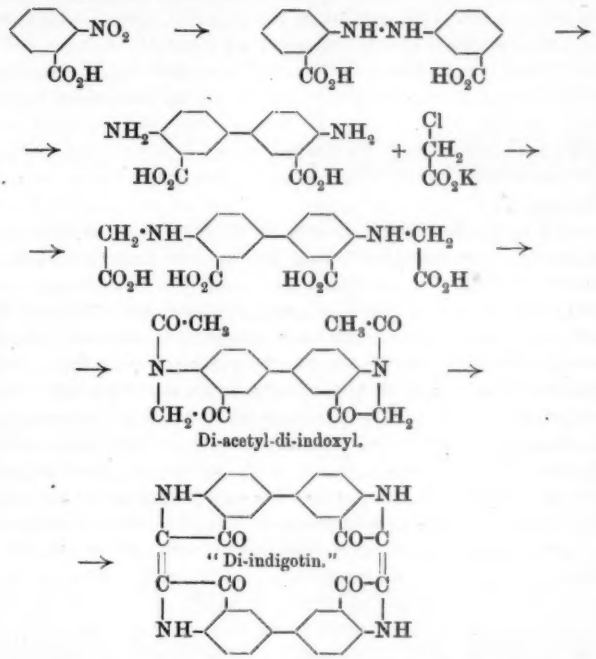


This was boiled during 4 hours with excess of acetic anhydride and dry potassium acetate, and finally taken to dryness on the water-bath. This process closes the indoxyl ring. The product freed from inorganic substances by washing, on digestion with dilute sodium hydroxide, dissolved, the solution becoming green, whilst a pellicle of the di-indigotin formed on the surface. Air was passed into the diluted solution and the olive-green substance was filtered off, washed, and dried. The filtrate was also dark green and gave on acidifying a dark green carboxylic acid, which probably results from the formation of the indoxyl ring at one end only of the first substance.

The properties of the di-indigotin precluded any exact investigation. It is only very slightly soluble in boiling *p*-toluidine, giving a solution distinctly bluer than the original substance as first prepared in fine

suspension. It gives an olive-green solution in concentrated sulphuric acid, but is apparently not sulphonated at 100°. It was not analysed, because it was impossible to guarantee its uniformity, but its stability precludes the possibility that it is merely a substituted indigotin.

The following scheme probably represents its formation :



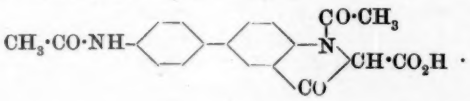
An attempt to confirm this by obtaining the same substance by another synthesis was made. All the methods involving potash fusion failed, but the method of Blank (*Ber.*, 1898, **31**, 1816) was partially successful and is here given as involving the preparation of a new substance. Benzidine was heated with a solution of half its weight of diethyl bromomalonate in chloroform until the odour of the former had gone ; the product was boiled out with chloroform and benzene and the filtered extracts concentrated and cautiously treated with ligroin, when the new ester crystallised out in plates. After two recrystallisations from ethyl acetate, it was white and melted sharply at 138°. An analysis showed it to be the expected *ethyl benzidino-dimalonate*, $\left[-C_6H_3-NH\cdot CH(CO_2Et)_2\right]_2$.

0·1564 gave 0·3542 CO_2 and 0·0918 H_2O. C = 61·73; H = 6·52.
0·2562 „ 12·80 c.c. moist nitrogen at 21° and 759 mm. N = 5·69.
$C_{26}H_{32}O_8N_2$ requires C = 62·40; H = 6·40; N = 5·60 per cent.

It forms minute, lustrous plates, sparingly soluble in alcohol and in cold benzene, easily so in hot benzene, ethyl acetate, and chloroform. It is slowly hydrolysed by alkalis, the solution giving, with acids, a flocculent precipitate of the corresponding acid.

On the analogy of Blank's indigo synthesis from ethyl anilinomalonate, the new ester was heated to 200° in an oil-bath until the evolution of vapour ceased. The product was dissolved in a little acetone, filtered, and precipitated by alcohol, giving a dark gum (whilst the alcoholic solution gave a little of the unchanged substance in needles, identified by mixed melting point). On boiling the gum with alcohol, a red resin was left, and the alcoholic solution was concentrated and hydrolysed by sodium hydroxide, giving a deep green solution, but no other evidence of the presence of di-indigotin in solid form. Evidently the action of heat on ethyl benzidinodimalonate is not analogous to its action on ethyl anilinomalonate, for many other temperatures than 200° were tried, but with even less success.

The author has prepared another new substance by boiling benzidine dicarboxylic acid with dry chloracetic acid and dry potassium chloracetate: carbon dioxide was split off, but the product was acetylated as in the former synthesis. A crystalline carboxylic acid (lance-shaped, white crystals, m. p. 292°) was isolated and recrystallised from boiling ethyl acetate. Analysis showed C = 64·94; H = 4·85; N = 7·91 hence the formula $C_{19}H_{16}O_5N_2$, and probably the constitution



153. "Note on the localisation of phosphates in the sugar cane." By C. H. G. Sprankling.

As very little work has been done with regard to the position of mineral constituents in plants, the author selected the sugar cane as a convenient plant to ascertain the position of the phosphates therein.

Equal portions of three sound canes were thoroughly dried, and after being ground to a fine powder, weighed quantities were ignited, using a slight modification of Fluckiger's method (*Zeit. anal. Chem.*, 1889, **27**, 637).

The ash in each case was extracted with dilute nitric acid, and the final ignited residue taken to be silica; the phosphates in the nitric acid solution were estimated.

From the results of his experiments, the author draws the following conclusions:

(*a*) Phosphates are immediately absorbed by the roots of the plant.

(*b*) These phosphates are rapidly transferred to the upper parts of the plant.

(*c*) A quantity of phosphates is stored in the upper portions and leaves of the cane.

(*d*) The silica is transferred regularly to the leaves, and there stored.

154. "On the non-existence of the gaseous sulphide of carbon described by Deninger." By E. J. Russell and N. Smith.

The authors have examined the gas prepared as Deninger describes (*J. für. Prak. Chemie*, 1895, ii, **51**, 346) and to which he gave the formula CS. Deninger prepared it (1) by heating together in a sealed tube chloroform and sodium sulphide, (2) by subjecting to the same treatment a mixture of iodoform and silver sulphide, (3) by the action of sodium on carbon disulphide mixed with aniline. The authors can find no evidence whatever of the existence of this gas. Sodium and carbon disulphide left in a closed apparatus fitted with a mercury gauge were found to produce no gaseous substance: a mixture of sodium, aniline, and carbon disulphide evolved hydrogen and hydrogen sulphide, and these gases in escaping carried over some carbon disulphide. Evidence that no other gas was present was obtained (1) by analysis, (2) by cooling the mixture and separating it into its constituents.

On heating together in a sealed tube to 180° a mixture of potassium sulphide and chloroform, the products were hydrogen sulphide, hydrogen chloride, chloroform, a reddish-yellow liquid which was apparently an alkyl sulphide, and free sulphur. A mixture of iodoform and silver sulphide similarly treated yielded hydrogen, carbon disulphide, and the reddish-yellow liquid. Although owing to the complex nature of these products the authors can hardly assert that no new gas having the formula CS was present, they could find no indication of any such compound.

155. "Hydroxyoxamides. Part II." By R. H. Pickard, C. Allen W. A. Bowdler, and W. Carter.

The authors described the following new hydroxyoxamides, namely: *o*-, *m*-, and *p*-nitrophenyl-, *o*-tolyl-, and ethyl-hydroxyoxamides. These react as hydroxamic acids (*Trans.*, 1901, **79**, 841). The esters of hydroxyoxamides are weak acids, and the hydroxyoxamides react with phenylhydrazine, forming phenylhydrazides. These and other reactions show

that the hydroxyoxamides behave like typical hydroxamic acids, and are therefore constituted according to the formula R·NH·CO·C(OH):NOH and not R·NH·C:(NOH)·CO_2H, as suggested by Schiff (*Annalen*, 1902, **321**, 357) and Holleman (*Rec. trav. chim.*, 1896, **15**, 148).

156. "Isometric anhydrous sulphates of the form $M''SO_4,R_2'SO_4$." By F. R. Mallet.

The author described the anhydrous salts $MgSO_4,K_2SO_4$, $MgSO_4,Rb_2SO_4$, $MnSO_4,K_2SO_4$, $MnSO_4,Rb_2SO_4$, $MnSO_4,Tl_2SO_4$, $NiSO_4,K_2SO_4$, and $CoSO_4,K_2SO_4$, which all crystallise in tetrahedral forms, being allied in this respect to the sulphates $2M''SO_4,R_2'SO_4$ previously described (*Trans.*, 1900, **77**, 216). They vary in their stability when exposed to the air, some remaining unaltered, whilst others are converted somewhat rapidly into the hexahydrated salts, $M''SO_4,R_2'SO_4,6H_2O$.

157. "The catalytic racemisation of amygdalin." By J. W. Walker.

Much more amygdalin is dissolved by water containing a small quantity of alkali, of alkaline earth, or of alkali carbonate, than by pure water. From polarimetric determinations of the rate of hydrolysis of the various substances involved, the author concludes that in alkaline solution the glucoside is racemised by the catalytic action of the hydroxyl ions, and that amygdalinic acid is racemoid with respect to its asymmetric carbon atom.

158. "On asymmetric optically active selenium compounds and on the sexavalency of selenium and sulphur." By W. J. Pope, F.R.S., and A. Neville, B.Sc.

Methylphenyl selenide, $C_6H_5{\cdot}Se{\cdot}CH_3$, the first mixed alkyl selenide which has been described, is obtained as a pale yellow oil boiling at 200—201° by the action of methyl iodide on the sodiophenyl selenide of Krafft and Lyons. Owing, apparently, to the highly basic character of selenium, it differs markedly from methylphenyl sulphide in that it combines readily with bromacetic acid to form the asymmetric *methylphenylselenetine bromide*, $\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!Se\!<\!\begin{matrix}Br\\CH_2{\cdot}CO_2H\end{matrix}$; this salt crystallises in colourless scales melting at 111° and on treatment with silver *d*-bromocamphorsulphonate, yields a mixture of the two following salts, which may be separated by crystallisation from alcohol.

d-*Methylphenylselenetine* d-*bromocamphorsulphonate* (*d-B*, *d-A*), $Se(CH_3)(C_6H_5)(CH_2{\cdot}CO_2H){\cdot}C_{10}H_{14}BrOSO_3$, is the less readily soluble

and forms needles melting at 168°; in aqueous solution, its rotations are $[\alpha]_D = +61{\cdot}26°$ and $[M]_D = +330{\cdot}8°$.

l-Methylphenylselenetine d-bromocamphorsulphonate (*l-B, d-A*); is much more soluble than the preceding salt, and is obtained in minute, white scales melting at 151°. Its rotations in aqueous solution are $[\alpha]_D = +38{\cdot}81°$ and $[M]_D = +209{\cdot}6°$. Since the *d*-bromocamphorsulphonic ion has the molecular rotation $[M]_D = +270°$, the corresponding value for the optically active selenetine ion is $[M]_D = \pm 60{\cdot}6°$.

The *dextro-* and *lævo-methylphenylselenetine platinichlorides*, $[Se(CH_3)(C_6H_5)(CH_2{\cdot}CO_2H)Cl]_2PtCl_4$, form yellow prisms melting at 171°; they have the molecular rotations $[M]_D = +55{\cdot}0°$ and $-54{\cdot}3°$ respectively in acetone solution.

The same optically inactive *methylphenylselenetine mercuriodide*, $Se(CH_3)(C_6H_5)(CH_2{\cdot}CO_2H)I,HgI_2$, is obtained by precipitating either of the salts (*d-B, d-A*), (*l-B, d-A*), or methylphenylselenetine bromide with a solution of potassium mercuric iodide; the mercuriodide forms white scales melting at 141—142°. The optical inactivity of this salt being remarkable, in view of the fact that the *d*- and *l*-benzylphenylallylmethylammonium ions preserve their optical activity during formation of the mercuriodides, it seemed desirable to ascertain if the same behaviour was exhibited during the formation of a mercuriodide from an optically active thetine.

The authors therefore prepared the optically active methylethylphenacylthetine salts of Smiles instead of the methylethylthetine compounds previously described by Pope and Peachey, owing to the greater optical rotations exhibited by the optically active ions of the former substances. It was then found that the *d*-methylethylphenacylthetine *d*-bromocamphorsulphonate, (*d-B, d-A*), had the molecular rotation $[M]_D = +332{\cdot}8°$, whilst the corresponding salt, (*l-B, d-A*), gave $[M]_D = +210{\cdot}6°$; the optically active methylethylphenacylthetine ion therefore has the molecular rotation $[M]_D = \pm 61{\cdot}1°$, a value about three times as great as $[M]_D = \pm 19{\cdot}4°$, the molecular rotation deduced from Smiles' determinations.

Each of the above salts yields the same optically inactive *mercuriodide*, $S(CH_3)(C_2H_5)(CH_2{\cdot}CO{\cdot}C_6H_5)I,HgI_2$, melting at 128°, and *mercurichloride*, $S(CH_3)(C_2H_5)(CH_2{\cdot}CO{\cdot}C_6H_5)Cl,HgCl_2$, melting at 119°. They also give the same *methylethylphenacylthetine-d-mercuribromocamphorsulphonate*, $S(CH_3)(C_2H_5)(CH_2{\cdot}CO_2{\cdot}C_6H_5)C_{10}H_{14}BrOSO_3,Hg(C_{10}H_{14}BrOSO_3)_2$, which has a molecular rotation $[M]_D = +799°$, very nearly three times that of the *d*-bromocamphorsulphonic ion, and in which the sulphur atom does not seem to act as a centre of optical activity.

The authors conclude that the mercuri-compounds of the sulphonium and selenonium bases probably contain sexavalent sulphur and selenium.

159. "The transformation of acetylchloroaminobenzenes into the isomeric chloroacetanilides." By F. D. Chattaway and K. J. P. Orton.

Owing to the recent publication by Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, p. 178) of measurements of the velocity of transformation of acetylchloroaminobenzene into *p*-chloroacetanilide, the authors wish to record the results of some preliminary experiments made by them two years ago (September, 1900) on isomeric changes of this type. These experiments were not published at that time, as Armstrong had previously stated (*Trans.*, 1900, **77**, 1053) that he was engaged on a similar investigation.

To follow the course of the isomeric change, a 1 per cent. solution of the chloramine in glacial acetic acid or in 50 per cent. acetic acid was kept at a constant temperature in the dark, and the amount transformed estimated at intervals by titrating the iodine liberated from hydriodic acid by the unchanged substance. In the presence of an acid, such as hydrochloric or sulphuric, the isomeric chloroacetanilide is produced. When hydrochloric acid is added, the change starts at once and proceeds regularly; with sulphuric acid, on the other hand, no transformation occurs at first, but after a short interval it begins and proceeds at a constantly increasing rate. At any period, however, during which isomeric change is taking place, hydrogen chloride can be recognised in the solution. The results of the authors confirm the observation first made by Armstrong (*loc. cit.*), that hydrochloric acid has a specific action in the transformation of phenylchloramines.

The experiments were carried out mainly with acetylchloroamino-*p*-chlorobenzene, $C_6H_4Cl{\cdot}NCl{\cdot}Ac$, not only because this substance is obtained somewhat more easily in a pure state, but especially because it changes more slowly into the isomeric anilide than does acetylchloroaminobenzene.

The value of the velocity coefficient, calculated from the equation $k = 1/t \log a/(a-x)$, increases with the amount of the catalytic agent and with the temperature, but decreases when the proportion of water in the solvent is increased. In any given experiment, it also begins to increase at some point in the course of the reaction, usually after the first 50 per cent. of the chloramine has changed.

The following experiment shows the kind of results obtained: A 1 per cent. solution of acetylchloroamino-*p*-chlorobenzene in glacial acetic acid containing 0·023 per cent. hydrogen chloride was kept at a temperature of 16·5°, and the unchanged chloramine estimated at the end of 1, 2, 4, 6, 8, 24, and 28 hours. Calculating the velocity coefficient from the above equation, the values obtained are respectively 0·0100, 0·0104, 0·0106, 0·0105, 0·0107, 0·0109, and 0·0110; the mean value is 0·0106.

In a series of experiments carrried out in order to ascertain the effect of temperature and of variation in the percentage of hydrogen chloride present, and in the concentration of the acetic acid, the following results were obtained. Using a 1 per cent. solution in glacial acetic acid containing 0·023 per cent. hydrogen chloride, half the chloramine was transformed in 27·4 hours; but in the presence of 0·069 per cent. hydrogen chloride, half was transformed in 5·33 hours, the temperature in each case being 16·5°. With a 1 per cent. solution containing 0·023 per cent. hydrogen chloride, at a temperature of 35·9°, half was transformed in 2·75 hours; the value of the velocity-coefficient in this case was not constant, but rapidly increased. Using 50 per cent. acetic acid containing 0·023 per cent. hydrogen chloride as the solvent, 120 hours elapsed before half was transformed at a temperature of 16·5°.

With 0·9 per cent. sulphuric acid, instead of hydrogen chloride, in glacial acetic acid, at a temperature of 16·5°, no appreciable change occurred in 2 hours; but after 24 hours 8·9 per cent., and after 84 hours 50 per cent., had changed. Hydrochloric acid, which could not be recognised in the solution after 2 hours, was found to be present after 24 hours.

Similar experiments made with acetylchloroaminobenzene, PhNCl·Ac, show that the isomeric change takes place at a greater rate when the chlorine can wander into the para-position than when it can only pass into the ortho-positions. Thus, in an experiment similar to those just described (HCl = 0·023 per cent.), the time required for the transformation of half the chloramine was 2 hours instead of 27·4 hours.

In connection with the transformation of phenylacylchloramines under the influence of hydrogen chloride, the following facts are worthy of note. When kept in the dark at the ordinary temperature, the titer of a solution in glacial acetic acid of acetylchloroamino-2 : 4-dichlorobenzene, which under these conditions cannot be transformed into the isomeric *s*-trichloroacetanilide, slowly falls, and at the same time a vapour (probably hypochlorous acid) is given off, which sets free iodine from potassium iodide. (A similar vapour is evolved from solution of any chloramine in glacial acetic acid.) If small quantities of hydrogen chloride or sulphuric acid be present, the titer decreases more rapidly; thus with a solution of the last-mentioned chloramine containing 0·069 per cent. of hydrogen chloride, the titer fell 23 per cent. at 16·5° in eight days, whilst in the presence of 0·36 per cent. sulphuric acid the titer fell 8 per cent. of the initial amount in the same period. In both cases the solutions, which were kept in the dark, acquired a yellow colour. Possibly these changes are due to the hydrolysis of the chloramine; the acetic acid contained 1·8 per cent. of water.

Further, when a solution of hydrogen chloride in dry petroleum is added to a solution of acetylchloroamino-*p*-chlorobenzene in the same solvent, *p*-chloroacetanilide, which is insoluble in petroleum, immediately separates.

Blanksma (*loc. cit.*) has drawn attention to the action of light in effecting this isomeric change, and has observed the transformation of the solid substances under its influence. On exposing any chloramine dissolved in chloroform or in acetic acid to sunlight, the originally colourless solution in a few minutes becomes yellow and acquires a chlorous smell; in all cases the solution then gives a precipitate with silver nitrate. If a phenylacylchloramine, which is capable of isomeric change, is so treated, transformation follows. Thus after two hours' exposure to sunlight, acetylchloroamino-*p*-chlorobenzene is changed into the isomeric anilide to the extent of 31 per cent. when dissolved in chloroform, but only to the extent of 12 per cent. when dissolved in acetic acid. The light is probably active by virtue of the fact that it induces decomposition, in the course of which the catalytic agent is formed.

These results show that in the presence of hydrogen chloride the transformation of phenylacylchloramines into chloroanilide is *apparently* a monomolecular reaction, and in this way resembles other similar isomeric changes; but it must not be forgotten that in measuring the speed of a chemical reaction the velocity of the slowest of the series of simple changes which constitute the complete transformation is alone measured.

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III. Pamphlets.

Agricultural Students' Gazette. Vol. x, part 2, Dec., 1900; and vol. x, part 6, April, 1902. From Professor Kinch.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before December 8th.

At the next meeting, on **Wednesday**, November 19th, at **5.30** p.m., the following papers will be communicated:

"The dynamic isomerism of thiourea and ammonium thiocyanate." By J. E. Reynolds and E. A. Werner.

"Isomeric partially racemic salts containing quinquevalent nitrogen. Part VIII. Resolution of the hydrindamine bromocamphor sulphonates." By F. S. Kipping.

"Isomeric compounds of the type $NR_1R_2H_3$." By F. S. Kipping.

"The synthesis of *aa*-dimethylglutaric acid, of *β*-hydroxy-*aa*-dimethylglutaric acid, and of the *cis*- and *trans*-modifications of *aa*-dimethylglutaconic acid." By W. H. Perkin, jun., and Miss E. Smith.

"A reaction of some phenolic colouring matters. Part II." By A. G. Perkin and C. R. Wilson.

"The vapour pressures and boiling points of mixed liquids. Part II." By S. Young and Miss E. C. Fortey.

"The vapour pressures and boiling points of mixed liquids. Part III." By S. Young.

"Note on mixtures of constant boiling point." By S. Young.

"Note on the condensation points of the thorium and radium emanations." By E. Rutherford and F. Soddy.

"The oxime of mesoxamide and some allied compounds. Part II. Disubstituted derivatives." By Miss M. A. Whiteley.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 26/11/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. No. 256.

Wednesday, November 19th, 1902. Professor EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs.:

Gilbert John Alderton, Eglinton Road, Plumstead, S.E.
Harry Percy Lewis, Swansea Hematite Works, Landore.
Thomas Samuel, School of Science and Art, Liscard, Cheshire.
John Mello Wadmore, B.A., Meriden, Exmouth.
Albert Wilmore, 158, Skipton Road, Colne.
William Wade Yeomans, Middlewich, Cheshire.

The PRESIDENT announced that the Council that afternoon had appointed Dr. G. T. Morgan to be Editor of the publications of the Society from January 1st next.

Of the following papers, those marked * were read:

***160. "The 'dynamic isomerism' of thiourea and ammonium thiocyanate." By J. E. Reynolds, D.Sc., F.R.S., and E. A. Werner, F.I.C.**

The method of producing thiourea for use in the arts is still essentially that by which one of the authors succeeded in isolating the substance in 1868 (*Trans.*, 7, 1). This consists in carefully

heating fused ammonium thiocyanate so as to secure as far as possible the molecular rearrangement represented by $NH_4CNS = CSN_2H_4$.

The proportion of thiourea actually formed at any *single* operation of this kind is known to be small. Volhard and others have variously estimated the yield at 15 to 22 per cent. of the thiocyanate taken for conversion. It is also well known that pure thiourea, when melted, slowly reverts to ammonium thiocyanate; but the estimates of the extent of this reversion also vary considerably. Viewed as a "balanced action" conditioned by heat alone, these changes are cited by Lowry as examples of "dynamic isomerism."

In view of these discrepancies which they considered were probably due to the use of small quantities of impure or moist materials, the authors have systematically studied on a comparatively large scale the effects of temperature and time on the course of these changes, and give the results of their experiments in curves. They show that:

1. Ammonium thiocyanate fused and then raised to, and maintained at, a steady temperature of 170°, underwent gradual change into thiourea until a maximum of 24·7 per cent. was reached after 45 minutes. Continued heating for 25 minutes longer led to slight *loss* of thiourea by decomposition.

2. In another series of experiments, the mean temperature being 182°, similar results were obtained, but the change was more rapid in the earlier stages, although the time required for the maximum effect was substantially the same as before.

3. Pure thiourea fused, and then maintained at a steady temperature of 170°, gradually reverted to ammonium thiocyanate, and after 40 minutes only 25·8 per cent. of thiourea remained. That proportion was not materially diminished by continued heating.

Therefore equilibrium is reached from either side when the isomerides are present in the melt in proportions which are substantially 25 per cent. of thiourea and 75 per cent. of ammonium thiocyanate, which is the composition of a definite compound having the formula $CSN_2H_4,(NH_4CNS)_3$.

The authors conclude that the arrest of change is due to the production of this compound which appears to be more stable at high temperatures than either of its constituents.

In confirmation of this view, they find that crystalline aggregates of nearly the above composition can be separated from the centre of a slowly cooled mass, produced by heating about a kilogram of ammonium thiocyanate to 170° for 40 minutes.

Further, having noted that the material which contained about 25 per cent. of thiourea remained liquid down to 106°, they determined the points of complete liquefaction of a number of very intimate mixtures of pure thiourea and thiocyanate. They found that there

was a regular decrease in melting point from 148° (that of pure thiocyanate) to 106°, at which latter temperature a mixture containing 25 per cent. of thiourea fused, but with still higher percentages of thiourea there was a regular *rise* in melting point, as shown on a curve of eutectic form having its minor point at 106°.

Finally, it was pointed out that the dissociation of the high temperature compound by solvents is by no means complete unless the latter are used in comparatively large proportions. Thus, when the melt was treated with insufficient warm acetone to dissolve it wholly, the solution afforded a compound which afterwards separated in feathery groups of crystals. This substance proved on analysis to be CSN_2H_4,NH_4CNS. With alcohol and water, the process of breaking down proceeds farther, but even warm water, if used in small proportion, does not cause complete separation, as fine, long crystals were easily obtained from such a solution which consisted of $(CSN_2H_4)_3,NH_4CNS$.

This compound is obviously complementary in composition to that which is formed in the fused mass at 170°. Re-solution of the crystals in water leads to complete separation.

Generally, the authors conclude that the state of equilibrium reached when either isomeride is heated to 170° for 40 minutes is conditioned as much by perfectly definite chemical attraction as by heat.

***161. "Isomeric partially racemic salts containing quinquevalent nitrogen. Part VIII. Resolution of the hydrindamine bromocamphorsulphonates." By F. S. Kipping.**

In previous communications (*Trans.*, 1900, **77**, 861; 1901, **79**, 430), the author has described several cases of a new type of isomerism observed in the study of salts of *dl*-hydrindamine (and of *dl*-benzylhydrindamine) with bromo- and chloro-camphorsulphonic acids and with *cis*-π-camphanic acid; in order to account for the existence of these isomerides, it was assumed that each of the optically active bases gives rise to *two* salts, and that the four compounds thus formed unite in pairs to produce the two partially racemic isomerides.

Further investigation, which so far has been restricted to the isomeric hydrindamine bromocamphorsulphonates (distinguished as the 'α'- and 'β'-salts), seems to show that this view of their nature is substantially correct.

Resolution of the α-Salt.—When the α-salt (m. p. 150°), which separates unchanged from most ordinary solvents, is heated with a little ethyl acetate under suitable conditions, it is resolved into two com-

ponents, one of which is deposited from the hot solution, whilst the other can be isolated from the mother liquors. The former, provisionally called the αA-salt, crystallises in needles melting at about 223°; the latter, the αB-salt, crystallises in needles melting at about 130°.

These two salts have practically the same specific rotation in dilute aqueous solution, namely, $[\alpha]_D = +60°$; the molecular rotation, therefore, in both cases is +266°, a value identical with that of bromocamphorsulphonic acid. The two compounds represent, nevertheless, salts of the enantiomorphously related hydrindamines, the bases having such low molecular rotations that they show no appreciable activity, even in moderately concentrated solutions of their hydrochlorides. The hydrochlorides, prepared from the αA- and αB-salts, are identical in ordinary properties, but the salts obtained by combining the bases from αA and αB with optically active acids are different; it follows, therefore, that the enantiomorphously related bases do not undergo racemisation when liberated from their salts.

Resolution of the β-Salt.—The partially racemic β-salt (m. p. 130°) is also resolved into different components when it is crystallised from hot ethyl acetate under suitable conditions. The salt, which separates from the hot solution, crystallises in needles which appear homogeneous and which resemble αA very closely in outward and in optical properties; when, however, this compound is systematically crystallised from water, after some 30—40 operations, it is further resolved into a salt identical with αA and a new isomeride βA; the latter is very similar to αA, but melts at a lower temperature (about 215°), and has a lower specific rotation ($[\alpha]_D = +56°$) in aqueous solution; it is possible that this salt may not have been obtained quite free from αA.

The ethyl acetate mother liquors, from which αA and βA have been deposited, contain unchanged β-salt together with two isomerides; one of these is identical with αB, but the other, βB, although very similar to αB in some properties, can be separated from it by fractional crystallisation from water. This fourth isomeride, βB, melts at about 130° and has a specific rotation $[\alpha]_D = +39{\cdot}5°$ in aqueous solution.

Synthesis of the α- and β-Salts.—When equal quantities of αA and αB are dissolved together in hot water, the solution deposits the partially racemic α-salt, and fractional crystallisation fails to reveal the presence of any β-salt in the product.

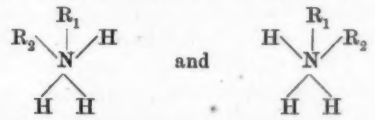
When αA and αB are separately decomposed with baryta and the liberated bases are neutralised with the bromo-acid, the salts obtained appear to be identical with αA and αB respectively, but they are not so; for if now mixed in equal quantities and crystallised from water they give a product which consists of a mixture of the α- and β-partially racemic salts. This is because, on uniting with the acid, the

one base gives αA and βA, the other αB and βB; the salt produced by combining the base from αB with the acid may, in fact, be resolved into αB and βB by fractional crystallisation.

When equal quantities of βA and βB are dissolved together in water, there results a salt which crystallises in hydrated prisms, indistinguishable in appearance from those of the partially racemic β-salt (m. p. 130°), but which, when dehydrated, melts at about 165°; this fact, and the constant occurrence of four compounds in the products of the resolution of samples of the β-salt which have been repeatedly crystallised to free them from α-salt, show that the β-salt is composed of *four* isomerides. The salt composed of equal quantities of βA and βB seems to represent a new isomeride, in which case there would be three partially racemic salts.

***162. "Isomeric compounds of the type $NR_1R_2H_3$." By F. S. Kipping.**

From the results summarised in the preceding note, it will be seen that *six* isomeric salts have now been isolated from the mixture produced by the combination of *dl*-hydrindamine and *d*-bromocamphorsulphonic acid. Four of these salts, αA, αB, βA, and βB contain one molecule of one of the enantiomorphously related bases combined with one molecule of the acid, that is to say, each of the bases gives rise to two isomerides which may be represented by the symbols:



Such compounds, containing only *three* different radicles united with quinquevalent nitrogen, afford an example of a type of isomerism hitherto unknown; it is possible, however, that the isomerism of the optically inactive compounds of the type $NR_1R_2R_3R_4R_5$, described by Wedekind, may be of an analogous character.

The existence of these new isomerides has no doubt an important bearing on the question of the arrangement in space of the groups around a quinquevalent atom, and would seem to exclude the double tetrahedron configuration; also the view, very generally held, that the negative ion in an ammonium salt takes up one particular valency. The fact that, in the case examined, the two radicles R_1 and R_2 are enantiomorphous does not of course preclude the possibility of the existence of isomerides in which the three different radicles are all optically inactive, and it may even be possible that an apparently

simple salt, such as ammonium chloride, is in reality a mixture of two isomerides.

One particularly striking fact in connection with the isomeric hydrindamine salts is their stability; all the four simple isomerides have been repeatedly crystallised from boiling water and other solvents, and hitherto the conversion of one into the other has never been observed.

It is also interesting to note the highly abnormal molecular rotation of the βB-isomeride; in 2 per cent. aqueous solution, $[M]_D = +175°$, whereas that of the acid is $[M]_D = +270°$. Since the ordinary base ion, although enantiomorphous, has only an extremely low molecular rotation, it might be inferred that the βB-isomeride is only very partially dissociated, and that there are two distinct types of ammonium salts.

***163. "The oxime of mesoxamide and some allied compounds. Part II. Disubstituted derivatives." By Miss M. A. Whiteley, D.Sc.**

The following mono- and di-substituted derivatives of the oxime of mesoxamide have been prepared: iso*nitrosomalondimethylamide*, m. p. 157°, the *potassium* and *ferrous* salts; iso*nitrosomalonanilide*, m. p. 141°, the *potassium*, *ferrous*, and *silver* salts; iso*nitrosomalondi-p-tolylamide*, m. p. 170—171°, the *potassium* and *silver* salts; iso*nitrosomalonmono-p-tolylamide*, m. p. 183°; iso*nitrosomalondi-o-tolylamide*, m. p. 111°, the *potassium* salt; *ethyl* iso*nitrosomalon-o-tolylamate*, m. p. 140—141°; iso*nitrosomalondi-α-naphthylamide*, m. p. 184°, the *potassium* salt; iso*nitrosomalondi-β-naphthylamide*, m. p. 221°, the *acetyl* derivative, m. p. 179°, a chlorinated derivative, m. p. 202°.

All these compounds possess the characteristic salt-forming properties exhibited by the original oxime, the alkali salts being yellow and the ferrous salts purple or blue. An interesting tautomerism is exhibited by some of them, the two isomerides differing from one another in colour (one being yellow and the other colourless), crystalline form, and solubility. The most probable explanation of this tautomerism is the assumption that the colourless isomeride has the *iso*oximino-structure, whilst the yellow isomeride and the yellow salts correspond to the oximino-compound.

The examination of a fairly extensive series of α-oximino-ketones has shown that in addition to the well known characteristic yellow coloration with alkalis, almost all give a deep purple or blue colour on the further addition of ferrous sulphate. This latter characteristic, however, appears to be influenced by the isomerism of the oximino-group, for α-benzil monoxime gives the reaction, whilst the β-isomeride does not. Again, among the dioximes, a considerable number, including α-benzil

dioxime, were found to give a deep purple or brown coloration with ferrous sulphate and an alkali, whilst β- and γ-benzil dioxime gave no coloration under these conditions.

***164. "Interaction of ketones and aldehydes with acid chlorides—the formation of benzoxyolefines and 1-benzoxycamphene." By F. H. Lees.**

The author has found that methyl *n*-nonylketone and benzoyl chloride readily interact when boiled together, forming *β-benzoxyundecylene* (α or β), $CH_2{:}C(OBz)\cdot C_9H_{19}$ or $CH_3\cdot C(OBz){:}CH\cdot C_8H_{17}$. It is an oil, b. p. 233—235° (50 mm.), and is regarded as being formed according to the scheme:

$$\begin{matrix}CH_3\\C_9H_{19}\end{matrix}\!\!>\!CO + C_6H_5\cdot CO\cdot Cl = \begin{matrix}CH_3\\C_9H_{19}\end{matrix}\!\!>\!C\!<\!\begin{matrix}O\cdot CO\cdot C_6H_5\\Cl\end{matrix} \rightarrow$$

$$(\alpha)\ \begin{matrix}CH_2\\C_9H_{19}\end{matrix}\!\!>\!C\cdot O\cdot CO\cdot C_6H_5 \text{ or } (\beta)\ \begin{matrix}CH_3\\C_8H_{17}\cdot CH\end{matrix}\!\!>\!C\cdot O\cdot CO\cdot C_6H_5 + HCl.$$

This formation of β-benzoxyundecylene represents the first instance of the direct transformation of a mono-oxygenated ketone into a derivative of its enolic form. The author has extended this reaction to other ketones, an aldehyde, and an aliphatic acid chloride, the following substances resulting: *β-benzoxynonylene* (α or β), $CH_2{:}C(OBz)\cdot C_7H_{15}$ or $CH_3\cdot C(OBz){:}CH\cdot C_6H_{13}$, from methyl *n*-heptylketone and benzoyl chloride, b. p. 210—211° (50 mm.); *β-benzoxy-γ-methylheptylene* (α or β), $CH_2{:}C(OBz)\cdot CH(CH_3)\cdot C_4H_9$ or $CH_3\cdot C(OBz){:}C(CH_3)\cdot C_4H_9$, from methyl *sec.*-hexylketone and benzoyl chloride, b. p. 197—200° (50 mm.); *β-benzoxyhexylene* (α or β), $CH_2{:}C(OBz)\cdot C_4H_9$ or $CH_3\cdot C(OBz){:}CH\cdot C_3H_7$, from methyl *n*-butylketone and benzoyl chloride, b. p. 170—175° (50 mm.); *α-benzoxy-α-phenylethylene*, $C_6H_5\cdot C(OBz){:}CH_2$, from acetophenone and benzoyl chloride, b. p. 227—230° (50 mm.); *1-benzoxycamphene*, $C_8H_{14}\!<\!\begin{matrix}CH\\\|\\C\cdot OBz\end{matrix}$, from camphor and benzoyl chloride, b. p. 215—220° (50 mm.); *α-benzoxy-α-heptylene*, $C_5H_{11}\cdot CH{:}CH(OBz)$, from œnanthaldehyde and benzoyl chloride, b. p. 195° (50 mm.); *β-valeroxyundecylene* (α or β), $CH_2{:}C(O\cdot CO\cdot C_4H_9)\cdot C_9H_{19}$ or $CH_3\cdot C(O\cdot CO\cdot C_4H_9){:}CH\cdot C_8H_{17}$, from methyl *n*-nonylketone and valeryl chloride, b. p. 185—190° (50 mm.).

Acetone with benzoyl chloride, and methyl nonylketone with acetyl chloride, did not interact; methyl *n*-propylketone and benzoyl chloride interacted only slightly. All the substances prepared are nearly colourless and odourless oils, and in their chemical properties exactly resemble each other. They all readily absorb bromine, form-

ing dibromo-addition products, and are unstable to potassium permanganate. The possibility of benzoxycamphene having a structure analogous to hydroxycamphene (Forster, *Trans.*, 1902, **81**, 264) was considered, but the fact that benzoxycamphene is readily hydrolysed by alcoholic hydroxylamine, yielding *l*-rotatory camphoroxime, and that its dibromo-addition product readily splits up into α-bromocamphor and benzoyl bromide, definitely proves the correctness of the structure $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot OBz\end{matrix}$.

65. "**The synthesis of** *aa*-**dimethylglutaric acid, of** *β*-**hydroxy**-*aa*-**dimethylglutaric acid, and of the** *cis*- **and** *trans*-**modifications of** *aa*-**dimethylglutaconic acid.**" **By W. H. Perkin, jun., and Miss A. E. Smith.**

When a mixture of ethyl dimethylmalonate and ethyl acetate is treated with sodium, condensation readily takes place with the formation of ethyl *aa*-dimethylacetonedicarboxylate, $CO_2Et\cdot CMe_2\cdot CO\cdot CH_2\cdot CO_2Et$, which distils at 185—190° (100 mm.) and gives, in alcoholic solution with ferric chloride, a red-violet coloration. When this ester is reduced with sodium amalgam and then with hydriodic acid, it yields the following acids:

β-Hydroxy-aa-dimethylglutaric acid, $CO_2H\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CO_2H$, which crystallises from water in prisms and melts at 158—160°.

aa-Dimethylglutaric acid, $CO_2H\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CO_2H$, which melts at 90° and is identical with the acid of this constitution obtained from *iso*lauronolic acid by oxidation with nitric acid.

cis-aa_1-*Dimethylglutaconic acid*, $CO_2H\cdot CMe_2\cdot CH{:}CH\cdot CO_2H$. This acid is readily soluble in water and melts at 134°; it combines with bromine yielding cis-$a_1\beta$-*dibromo-aa-dimethylglutaric acid* (m. p. 150°). When hydroxydimethylglutaric acid is distilled, it is, in part, converted into the sparingly soluble *trans*-aa_1-dimethylglutaconic acid which melts at 172° and was first obtained (Perkin, *Trans.*, 1902, **81**, 253) by the hydrolysis of ethyl a_1-bromo-*aa*-dimethylglutarate, $CO_2Et\cdot CMe_2\cdot CH_2\cdot CHBr\cdot CO_2Et$, with alcoholic potash. This same acid is obtained almost quantitatively from the above hydroxy-acid by treatment with phosphorus pentachloride, then with alcohol, and finally with alcoholic potash, $CO_2Et\cdot CMe_2\cdot CHCl\cdot CH_2\cdot CO_2Et$, giving $CO_2H\cdot CMe_2\cdot CH{:}CH\cdot CO_2H$. The *trans*-acid is acted on only with difficulty by bromine with formation of *trans*-$a_1\beta$-dibromo-*aa*-dimethylglutaric acid (m. p. 217°). It appears, therefore, that the *cis*- and *trans*-modifications of *aa*-dimethylglutaconic acid melt respectively at 134° and 172°. The bearing of this on the work of Conrad and of Henrich on this subject was discussed.

166. "A reaction of some phenolic colouring matters. II." By A. G. Perkin and C. R. Wilson.

By means of alcoholic potassium acetate, gallacetophenone gives the salts (*a*) $C_8H_7O_4K,H_2O$, and (*b*) $C_{24}H_{23}O_{12}K$. The former, pale yellow needles, identical with the compound which Nencki and Sieber (*Journ. pract. Chem.*, [ii], **23**, 23, 546) prepared with alcoholic potash, is anhydrous at 160°, and gives the salt $C_{16}H_{14}O_8Ba$, yellow needles. Sodium acetate gives the salt $C_8H_7O_4Na,H_2O$. With methyl iodide this gives *gallacetophenonemethyl ether*, $C_8H_7O_3(OCH_3)$, needles, m. p. 132—133°, the *diacetyl* derivative of which melts at 146—148°; and on methylation gallacetophenonedimethyl ether, m. p. 77—78°, (*Trans.*, 1895, **67**, 997) is formed. It is thus a para- or meta-methoxy-compound. The salt (*b*), colourless needles, is also formed from gallacetophenone and potassium acetate in aqueous solution and from this the compound $C_{48}H_{46}O_{24}Ba$ can be obtained.

The following salts have been prepared with alcoholic potassium acetate. Ellagic acid gives $C_{14}H_5O_8K$ and $C_{14}H_4O_8K_2$, daphnetin, $C_9H_6O_4,KC_2H_3O_2$, galangin, $C_{15}H_9O_5K,H_2O$, kampheride, $C_{16}H_{11}O_6K,H_2O$, dihydroxybenzalcumaranone (OH : OH = 6 : 7), $C_{15}H_{10}O_4,KC_2H_3O_2$, carminic acid, $C_{11}H_{11}O_6K$ and $C_{22}H_{22}O_{12}Ba$, styrogallol, $C_{16}H_7O_5K$, naphthazarine, $(C_{10}H_6O_4)_2,KC_2H_3O_2$?, and curcumin, $C_{21}H_{19}O_6K$. By means of alcoholic potash, daphnetin gives the salts $C_{18}H_{11}O_8K$ and $C_9H_5O_4K$, and carminic acid the salt $C_{22}H_{23}O_{12}K$. From acetyl rhamnetin, the compound $C_{16}H_{11}O_7K$ was obtained.

Dimethoxyanhydroglycogallol, $C_{10}H_{10}O_4$, yellow needles, m. p. 122°, gives with protocatechuic aldehyde *dimethoxydihydroxybenzalcumaranone*, $C_{17}H_{14}O_6$, orange-coloured needles, which with potassium acetate gives the salt $C_{17}H_{13}O_6K$. *Pyrogallolmonomethyl ether*, incidentally prepared, melts at 102—104°, and not at 95° as given by Benedikt (*Ber.*, 1877, **9**, 125).

167. "Note on mixtures of constant boiling point." By S. Young, D.Sc., F.R.S.

It was noticed by Thorpe (*Trans.*, 1879, **35**, 544) that when a mixture of equal volumes of carbon tetrachloride and methyl alcohol is distilled a mixture of minimum boiling point, 55·6—55·9°, comes over first. The vapour density of this distillate was found to be 41·82, and the composition was therefore

Carbon tetrachloride	78·1
Methyl alcohol	21·9
	100·0

At Dr. Thorpe's suggestion, the author has determined the composition of the mixture of minimum boiling point by the distillation method, and also from the specific gravity of the mixture after redistillation.

The results are as follows:

Distillation Method.

	From excess of CH_3OH.	From excess of CCl_4.	From specific gravity.
CCl_4	79·99	79·35	79·44
CH_3OH	20·01	20·65	20·56
	100·00	100·00	100·00

The separation of the mixture of minimum boiling point from methyl alcohol is very much more difficult than from carbon tetrachloride, and it is in all probability for this reason that the percentage of alcohol in Thorpe's distillate was too high, whilst that calculated from the results of the distillation of a mixture containing excess of alcohol was too low. The most accurate value is probably that deduced from the specific gravity of the redistilled mixture of constant boiling point.

Determinations by Thayer (*Journ. Phys. Chem.*, 1898, **2**, 382), Ryland (*Amer. Chem. Journ.*, 1899, **22**, 384), and Carveth (*Journ. Phys. Chem.*, 1902, **6**, 248) of the boiling points and composition of mixtures of benzene with ethyl and methyl alcohol were compared with those of Miss Fortey and the author (*Trans.*, 1902, **81**, 739).

168. "The Vapour pressures and boiling points of mixed liquids. Part II." By S. Young, D.Sc., F.R.S., and Miss E. C. Fortey, B.Sc.

In a previous paper (*Trans.*, 1902, **81**, 752) it was shown that, so far as mixtures of chlorobenzene and bromobenzene are concerned, the conclusion of van der Waals is true that if the critical pressures of the two liquids are equal and if the relation suggested by Galitzine and by Berthelot, $a_{1,2} = \sqrt{a_1 a_2}$ holds good, the relation between vapour pressure and molecular composition should be represented by a straight line, or the vapour pressures of mixtures may be expressed by the formula $P = \frac{pP_A + (100-p)P_B}{100}$, where P, P_A, and P_B, are the vapour pressures of the mixture and of the two components A and B at the same temperature, and p is the molecular percentage of A.

It does not, however, follow that it is only when the critical

pressures are equal that the vapour pressures agree with the formula; indeed Speyers goes so far as to state that it is always applicable to mixtures of liquids of normal molecular weight.

As the statement of Speyers is certainly too general, it seemed desirable to determine the boiling points of mixtures of a number of closely related compounds the critical pressures of which are not equal.

Four pairs of such liquids were examined, (1) ethyl acetate and ethyl propionate, (2) toluene and ethyl benzene, (3) *n*-hexane and *n*-octane, (4) benzene and toluene, and, in addition, carbon tetrachloride and benzene.

The investigation resulted in the following conclusions :—

1. The volume and temperature changes on mixing closely related substances are in all the observed cases very small, but it is only with chlorobenzene and bromobenzene that they can certainly be said to be within the limits of experimental error. With the two esters, these limits are very closely approached, whilst with benzene and toluene, which are somewhat less closely related, the changes are distinctly larger, and for mixtures of benzene with *n*-hexane and with carbon tetrachloride they are very much larger.

2. The formula $P=\frac{pP_A+(100-p)P_B}{100}$ is nearly, if not quite, true for closely related liquids, even when the critical pressures are widely different; it is not true, however, as a rule, for mixtures of liquids of normal molecular weight such as benzene and *n*-hexane, or for benzene and carbon tetrachloride, which are not closely related.

Of the five pairs of closely related liquids examined, it is only chlorobenzene and bromobenzene which show absolutely no temperature or volume change on mixing, and for mixtures of which the vapour pressures are accurately given by the above formula, and it is only this pair of liquids which have the same critical pressure. The deviations in the other cases are, however, so small that it remains an open question whether equality of critical pressure is a necessary criterion for absolute agreement with the formula. It appears, at any rate, that equality of critical pressure without closeness of chemical relationship is not a sufficient criterion.

It may be stated definitely that in the case of closely related substances, whatever their critical pressures, the deviations are, as a rule at any rate, exceedingly small.

Lastly, it is shown that there is strong evidence for the existence of mixtures of minimum boiling point in the case of carbon tetrachloride and benzene, and also of *n*-hexane and benzene, although the boiling points of the mixtures could hardly be distinguished from those of

carbon tetrachloride and *n*-hexane respectively by ordinary thermometric methods.

169. "The vapour pressures and boiling points of mixed liquids. Part III." By S. Young, D.Sc., F.R.S.

If the vapour pressures of mixtures of two liquids, A and B, are accurately expressed by the formula $P=\frac{pP_A+(100-p)P_B}{100}$ (where P, P_A, and P_B are the vapour pressures of the mixture and of the two components respectively at the same temperature, and p is the molecular percentage of A), and if the difference between P_A and P_B is small, the relation between the boiling points of the mixtures at constant pressure and their molecular composition is represented by a nearly straight line, and the temperature may with small error be calculated by means of the formula $t=t_B+\frac{p}{100}(t_A-t_B)$. The greater the difference between P_A and P_B, the greater is the deviation of the boiling point-composition curve from a straight line, and the higher is the molecular percentage of A in that mixture which shows the maximum deviation, D. This percentage is given with fair accuracy by the formula $p_D=50+0{\cdot}18\Delta$ (where Δ is the difference between the boiling points of A and B), and the maximum deviation may be calculated with very slight error from the formula

$$D_2=-\frac{0{\cdot}000158\Delta^2}{c'.T'}\cdot\frac{c_A}{c_B},$$

where c_A and c_B are the values of $\frac{dt}{dp}\cdot\frac{1}{T}$ for the two components

$$c'=\frac{(50+0{\cdot}18\Delta)c_A+(50-0{\cdot}18\Delta)c_B}{100}$$ and

$$T'=\frac{(50+0{\cdot}18\Delta)T_A+(50-0{\cdot}18\Delta)T_B}{100}.$$

The values of D_2, calculated from the above formula, and of D_1, deduced from the actual vapour pressures (*Trans.*, 1902, **81**, 752) for nineteen pairs of closely related compounds, were shown in a table. The greatest difference between D_2 and D_1 is 0·16°, although the actual value of D_1 is in one case − 32·8°. The boiling point curves have been determined experimentally in five cases, and the maximum deviation, D_3, read from the curves; the greatest difference between D_3 and D_1 is 0·27°.

For mixtures of liquids which are not closely related, the formula $P=\frac{pP_A+(100-p)P_B}{100}$ is not, as a rule, applicable, but if the ratio $\frac{c_A}{c_B}$

lies between 0·95 and 1·05 (probably between 0·9 and 1·1), D_2 agrees well with D_1, and in other cases the difference rarely amounts to one degree. The observed boiling points of mixtures differ, however, as a rule, from those deduced from the vapour pressures, more especially when the molecules of one or both liquids are associated.

Whether a mixture of constant boiling point can be formed or not depends chiefly on the relative values of Δ and $D_3 - D_1$. If Δ is very small, such a mixture may be formed even when the difference between D_3 and D_1 is less than 1°, as in the case of carbon tetrachloride and benzene ($\Delta = 3{\cdot}44°$, $D_3 - D_1 = -0{\cdot}89°$). On the other hand, methyl alcohol and water do not form such a mixture, although $D_3 - D_1 = -4{\cdot}95°$, Δ having in this case the high value 35·11°.

170. "Note on the condensation points of the thorium and radium emanations." By E. Rutherford and F. Soddy.

It was shown (*Trans.*, 1902, **81**, 342) that the radioactive emanation from thorium compounds passed in unchanged amount through a tube cooled to −78° with solid carbon dioxide and ether. The acquisition of a liquid air plant has enabled the authors to repeat the experiment at a lower temperature, with the result that they have now succeeded in condensing both the thorium and the radium emanations.

A current of hydrogen (or of air) was passed through the thorium or radium compound, and thence through a copper spiral cooled in liquid air. No trace of emanation escaped in the issuing gas either in the case of radium or of thorium. At the temperature of liquid air the emanations are therefore either condensed or lose their activity.

The radium (or thorium) compound was then removed, and the gas current sent directly through the spiral tube, which was quickly taken out of the liquid air and placed in cotton cool. Nothing happened for two or three minutes as the temperature of the spiral slowly rose, until suddenly the presence of the emanation was observed in large amount in the escaping gas. The result therefore cannot be explained by supposing that the emanations lose their ionising power at the temperature of liquid air. It is clear that they are condensed and again volatilised. From the sharpness and suddenness of the phenomena there appeared to exist for each emanation a definite temperature of volatilisation. This temperature is very nearly the same in the two cases and considerably above the boiling point of liquid air.

By measuring the temperature of the copper spiral at the instant of volatilisation, it was found that successive determinations agreed

amongst themselves to within a degree. The exact temperatures cannot yet be given, but as a first approximation it may be said that for the radium emanation the volatilisation point lies in the neighbourhood of −130° and for the thorium emanation about five degrees lower.

This experiment furnishes an additional proof—if such were needed—that radioactivity is accompanied by the continuous production of special kinds of active matter, which possess distinct and sharply defined chemical and physical properties.

171. "Note on the action of barium hydroxide on dimethylvioluric acid." By Miss M. A. Whiteley, D.Sc.

When dimethylvioluric acid is decomposed by boiling with barium hydroxide, the chief product is *iso*nitrosomalondimethylamide, which crystallises in well developed prisms belonging to the monosymmetric system ($a : b : c = 1{\cdot}53394 : 1 : 0{\cdot}88680$; $\beta = 68°43'$); it melts at 157°, and yields a yellow potassium salt and a purple ferrous salt, both of which are crystalline. In addition to this compound, six other decomposition products can be isolated, one, melting at 239—240°, has not been identified, the other five are carbon dioxide, oxalic acid (as barium salts), monomethyloxamide, methylamine, and methylamine oxamate. Andreasch (*Monatsh.*, 1895, **16**, 17), who first examined this reaction, obtained only three products, namely, carbon dioxide, methylamine, and a crystalline compound melting at 228° which he identified as *iso*-nitrosomalondimethylamide; this investigation, however, indicates that it was probably an impure specimen of monomethyloxamide.

172. "The determination of strychnine and brucine in nux vomica." By E. Dowzard.

In order to determine the strychnine, the pure mixed alkaloids are dissolved in 50 c.c. of 2 per cent. sulphuric acid, 5 c.c. of nitric acid are added, and the mixture allowed to stand for 15 minutes, the solution is transferred to a separator containing 15 c.c. of ammonia (sp. gr. 0·890) and 10 c.c. of chloroform, the mixture is shaken for 5 minutes, the solvent separated, and the alkaline liquid again shaken with 10 c.c. of chloroform. The mixed chloroform washings are now shaken with 15 c.c. of dilute ammonia (1 c.c. of above mentioned strength, diluted to 45 c.c.), this is repeated twice, the chloroform evaporated off, and the residue dried at 100° until constant.

To determine the brucine, a standard brucine solution is required, which is made by dissolving 0·16 gram of anhydrous brucine and 0·16

gram of strychnine in 2 per cent. sulphuric acid and the solution made up to 100 c.c. Then 0·10 gram of the pure mixed alkaloids is dissolved in 50 c.c. of 2 per cent sulphuric acid, this solution and 50 c.c. of the standard are placed in two small beakers, 5 c.c. of nitric acid (sp. gr. 1·42) are added simultaneously to the contents of each beaker; the solutions are then transferred to the comparison troughs of a Gallenkamp colorimeter. Five minutes after adding the nitric acid, six readings are taken; from the average of these, the brucine is calculated.

Results were given which proved the accuracy of the determination made by both these methods.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before December 8th.

At the next meeting, on **Thursday**, December 4th, at 8 p.m., when there will be a Ballot for the Election of Fellows, the following papers will be communicated:

"The absorption spectra of metallic nitrates. Part II." By W. N. Hartley, D.Sc., F.R.S.

"The specific heats of liquids." By H. Crompton.

"The constitution of enolic benzoylcamphor." By M. O. Forster.

"Isomeric benzoyl derivatives from *iso*nitrosocamphor." By M. O. Forster.

"The constitution of the products of the nitration of *m*-acetoluidide." By J. B. Cohen and H. D. Dakin.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on **December 4th**, 1902.

Alder, John Frederick,

13, Priestwood Mansions, Highgate, N.

Headmaster of the Higher School, East Finchley, N. Inter.B.Sc. (Lond.), Qualified Science Teacher under Science and Art Department; two years Demonstrator at High School, Middlesbrough, three years Science Master, East Finchley Science School; Lecturer in Chemistry to the Middlesex County Council (Finchley Centre).

J. Archyll Jones. John Geo. Taylor.
Frederick Doyle. *George Dean.*

A. Greeves.

Beanes, Alfred Edward,

Moatlands, Paddock Wood, Kent.

Analytical and General Chemist at Falcon Works, Wallis Road, Hackney Wick. Formerly Chemical Student at King's College, London, under Professor J. M. Thomson.

R. L. Barnes. T. A. Lawson.
W. S. Simpson. F. Evershed.

R. Meldola.

Blair, Herbert,

No. 3, General Hospital, Kroonstad, O.R. Colony, or c/o Robert Blair, Solicitor, Harton Lodge, Harton, South Shields, England.

Compounder of Medicines, Analytical Chemist and Assayer; Student in Chemistry and Assaying at the Durham College of Science, Newcastle-upon-Tyne.

John C. Hewlett. P. Phillips Bedson.
Charles Mills. F. C. Garrett.
S. Hoare Collins.

Brincker, John Augustus Herman,

7, St. Mary's Terrace, Paddington, London, W.

Medical Officer to the Croydon Borough Fever Hospital, and Bacteriologist to the Croydon Borough. B.A. (Cantab; First Class Natural Science Tripos), 1896; B.A. (Univ. Cape of Good Hope—Honours in Mathematics and Science), M.B., B.C. (Cantab); M.R.C.S. (Eng.), L.R.C.P. (Lond.); D.P.H. (Cantab), D.P.H., R.C.P.S. England, Late Assistant to the Prof. of Chemistry, U.C.G.H.; Government Scholar in Chemistry, Univ. C.G.H.; Porter Student and Univ. Scholar, U.C.G.H.; Foundation Scholar St. John's College, Cantab. and Univ. Exhibitioner in Natural Science, St. Mary's Hospital.

James Moir. Edward A. Andrews.
Henry Kenwood. Arthur P. Luff.
Christopher Childs. *J. F. Braga.*
W. H. Corfield. *Samuel Rideal.*

Bryant, Vernon Seymour,

Camborne, Cornwall, England.

Chief Chemist to the Egyptian Salt and Soda Company, Natural Soda Works, Bir Hooker, Wadi Natron Estate, Lower Egypt. Senior Minor, and Foundation Scholar and Natural Science Prizeman of Downing College, Cambridge. B.A. Nat. Sci. Tripos, 1899.

W. J. Sell. John J. Beringer.
Ayerst Henham Hooker. Henry Jackson.
W. H. Lewis.

Carmichael, Thomas Burnell,

Parton, Whitehaven, at present living at 415, Walton Breck Road, Anfield, Liverpool.

Student with Messrs. A. Norman Tate & Co., Hackins Hey, Liverpool, Analytical Chemists. Previous to the above was a student in the

Laboratory of the Mossbay Hematite Iron and Steel Co.. Workington, Cumberland, with Mr. G. Valentine, Chief Chemist.

J. W. Clayton. T. Armistead Ward.
Wm. Hall Jowett. William Harrington.
Archd. Kitchin.

Cockle, Charles,

Peter Symonds' School, Winchester.

Science Master. Two years' training at the Royal College of Science, South Kensington; 1893—1895. 1st Class Honours, 1896, Practical Inorgan. Chem. Seven years' experience in teaching Chemistry in Secondary Schools: Dorchester Grammar School; Camberwell Grammar School; Peter Symonds' School, Winchester. My chief reason for being admitted is to secure the best literature on Chemistry.

M. O. Forster. H. Burrows.
G. T. Morgan. J. W. Hinchley.
W. Palmer Wynne.

Drought, James Justinian,

P.O. Box 4058, Johannesburg. Present address, Woodlands, Blackrock, Co. Dublin.

Assayer and Consulting Chemist. Member of the Chemical and Metl. Society of South Africa. Chief Assayer, the Lancaster Gold Mining Co., Krugersdorp. Cyanide Manager and Acting General Manager, the Nooitgedacht E. and G.M. Co., Lydenburg. Consulting Chemist to the Langlaagte Recovery Works, Ltd. Johannesburg.

W. N. Hartley. George T. Holloway.
J. Holms Pollok. *W. F. Cousins.*
W. E. Adeney.

Edlin, Edgar Leeder, B.A.,

Marsh Parade, Newcastle, Staffs.

Senior Science Master, the High School, Newcastle, Staffs. Formerly Science Exhibitioner at Merton College, Oxford, 1st Class in Honours Chemistry, Natural Science School, in June, 1900; now Senior Science Master, Newcastle, Staffs.

John Watts. J. E. Marsh.
W. W. Fisher. H. A. Miers.
V. H. Veley. H. L. Bowman.

Edwards, Walter Henry,

The Grammar School, Wellingborough, Northants.

School Master. Science Master, Wellingborough Grammar School since 1895.

H. Brereton Baker. R. H. Aders Plimmer.
Frank Clowes. R. T. Lattey.
Arthur H. Coote.

Green, George Felix Dudbridge,

Rosslea, 9 Ross Road, South Norwood, S.E.

Analytical Chemist. At present Assistant to Mr. Matthew J. Cannon, F.C.S. General and Scientific Education, Dulwich College, S.E., and Lycée Jansan, Paris. First year of Diploma Course at City and Guilds under Professor Henry Armstrong. Two years under Professor J. M. Thomson, King's College, W.C. Course of Bacteriology under Professor Cruickshank. Passed the Intermediate for A.I.C., July 1901. Now Assistant to Mr. M. J. Cannon, F.C.S.

John M. Thomson. D. Northall-Laurie.
Herbert Jackson. Matthew J. Cannon.
Patrick H. Kirkaldy. Robert Yates.
C. T. Kingzett.

Grimwade, Wilfred Russell,

Melbourne, Australia.

Manufacturing Chemist. Bachelor of Science of the Melbourne University.

Orme Masson. Robert N. Lennox.
Thomas Tyrer. *N. H. Martin.*
J. Lewkowitsch. *Walter F. Reid.*
J. Campbell Brown.

Gumersall, Edward,

Atbara, Sidcup, Kent.

Sub-Inspector Board of Education. Certificate for Associateship Course in Chemistry of Royal College of Science, London. Have been engaged in promoting the teaching of the subject under the Board of Education for the past eight years.

T. E. Thorpe. R. Meldola.
W. Palmer Wynne. A. E. Tutton.
Chapman Jones.

Hollingworth, David Vincent,

Aldred House, Crescent, Salford.

Analytical Chemist. Have had four years' training in Inorganic and Organic Chemistry, Coal Tar Products, &c., &c., at Royal Technical Institute, Salford. I have position as chief chemist at Stretford Gas Works, and desire to keep myself well informed in Modern Chemistry by perusal of the literature of the Chemical Society.

Jas. R. Appleyard. Ernest Clark.
J. R. Denison. *James Walker.*
John S. Lumsden.

Holt, Alfred, jun., B.A. (Camb.),

Crofton, Aigburth, Liverpool.

Research Student in the Owens College, Manchester. Studied Chemistry at Cambridge, and worked with Professor Moissan at the Sorbonne, and has published two papers in conjunction with M. Moissan on the preparation of two silicides of vanadium.

Harold B. Dixon. W. H. Perkin, jun.
Norman Smith. J. F. Thorpe.
D. L. Chapman. Francis V. Darbishire.

Hosking, Arthur Francis,

Roskear Villas, Camborne, Cornwall, England.

Chief Chemist of the Cyanide Works, and Reduction Plant of the Aruba Gold Concession, Limited, Aruba Island, D.W.I. 1891—1893 private student assistant to John J. Beringer, Esq., A.R.S.M., F.I.C., F.C.S., obtaining Honours in Chemistry and Metallurgy, South Kensington Exams. First position in Cornwall both years, and highest council prizes. 1893 to 1896 (three years), Demonstrator in Honours Chemistry, Metallurgy, and Assaying at the Camborne Mining Schools, Cornwall. During this period I made the complete analyses of rock formations for the Geological Surveys made by the President of the Cornwall Geological Society. I received the highest award of the Royal Cornwall Polytechnic Society for complete analyses with microscopic sections and diagrams of various strata from the bottom of the Dolcoath Tin Mine in Cornwall. Also, for a period of over a year I made the assays of white tin and arsenic productions of the Drakewall Tin, Copper, and Arsenic Mines in North Cornwall, to the thorough satisfaction of the mine and the arsenic refiners who were the buyers. July 1896 to end of 1898. Engaged as assistant manager and technical expert to the Cassinga Concession's Prospecting Expedition in Angola, South-west Africa. 1899 to April 1900. Special studies

and research work on working potass cyanide liquors, &c., at the Camborne Mining School Laboratory. During this period I was awarded the silver medal of the Mining Association and Institute of Cornwall and Devon for chemistry, metallurgy, and allied subjects. April 1900 to date. Chief chemist of the Cyanide Works and reduction Plant of the Aruba Gold Concession, Aruba Island, Dutch West Indies.

Thomas Blackburn. J. J. Beringer.
H. R. Beringer. *H. W. Hutchin.*

John Gill.

Jackson, Clements Frederick Vivian,
Brisbane.

Assistant Government Geologist of Queensland. Bachelor of Mining and Metallurgy (Sydney University, 1900); Student for three years in the Chemical and Metallurgical Laboratories, University of Sydney, under Prof. Liversidge and Mr. J. A. Schofield. First Class honours Quantitative and Qualitative Analysis; First Class honours General Chemistry; Second Class honours Metallurgy and Assaying; First Class honours Physics; Slade Prize for Practical Physics; Bachelor of Civil Engineering (Sydney University, 1895); Associate Member of the Institution of Civil Engineers (London).

A. Liversidge. Chas. Watkin.
J. A. Schofield. J. Brownlie Henderson.

Basil Turner.

Jardine, Douglas Kennedy, B.Sc.,
20, Doune Terrace, Kelvinside, Glasgow, N.

Analytical Chemist. Studied at Owens College for five years, 1894–1898, and later at the Laboratory of the City Analysts, Messrs. R. R. Tatlock and Thomson, 1899 till date. Work consisted of analyses of every class, Scientific and Commercial. Holds Degree of Bachelor of Science.

R. R. Tatlock. W. H. Perkin, jun.
H. B. Dixon. G. H. Bailey.

D. L. Chapman.

Leather, John Petty,
17, Carlton Road, Burnley.

Gas Engineer and Manager of Burnley Corporation Gas Works. Studied Chemistry under Profs. Roscoe and Schorlemmer, 1876—1879. Since then Assistant Manager and Chemist, and for last twelve years Engineer and Manager of Burnley Corporation Gas Works. Joint

author of paper (*Soc. Chem. Ind.*) on the Constitution of Gas Oils. At present engaged with Mr. Ross in a research on Borneo oil.

Raymond Ross. George Embrey.
Wilfred Irwin. Chas. J. Waterfall.
James Bertram Russell.

Lidbury, Frank Austin, M.Sc.,
Owens College, Manchester.

Demonstrator and Assistant Lecturer in Chemistry in the Owens College. Studied Chemistry at the Owens College (B.Sc., 1898), Research work with Prof. Ramsay and Prof. Ostwald. Has published, in the *Journal Chem. Soc.*, two papers, and one paper in *Zeit. Phys. Chem.*

Harold B. Dixon. J. F. Thorpe.
W. H. Perkin, jun. D. L. Chapman.
Norman Smith. Francis V. Darbishire.

Liotard, Ernest,
2, Rue de France, Nice, France.

Pharmacien de première classe, Membre de la Société chimique de Paris, de la Société de pharmacie de Moscou, de Médecine de Nice. Auteur du traité d'analyse des urines, des hüiles essentielles des essences antiseptiques, du manuel de pharmacologie, et de notes de chimie.

Alfred H. Allen. G. E. Scott-Smith.
Arnold R. Tankard. *G. T. W. Newsholme.*
L. Troost.

Logan, Thomas Stratford,
52, Kirkgate, Leeds.

Physician. Studied Chemistry and allied subjects at Queen's College, Belfast, and at Yorkshire College, Leeds; Experience of Public Health Chemistry in the Sanitary Department of Leeds Corporation.

H. M. Dawson. H. D. Dakin.
A. Turnbull. J. K. S. Dixon.
B. A. Burrell.

MacCallum, Douglas A.;

10, Midlothian Drive, Shawlands, Glasgow.

Manufacturing, Analytical, and Consulting Chemist. Office address: Central Chambers, 93, Hope Street, Glasgow. (1) Technical College, Student and Assistant to Chemical Professor there, 3 years. (2) Iron and Steel Works Chemist, and latterly Assistant Manager; analytical work; research and investigations in connection with practical working, &c., 13 years. (3) Manufacturing and consulting privately, 2 years. (4) Member Society of Chemical Industry and West of Scotland Iron and Steel Institute.

A. Humboldt Sexton. James McCracken.
R. R. Tatlock. *John Clark.*
R. T. Thomson. *G. G. Henderson.*

Mann, William, B.Sc. (Lond.),

Fonnereau Villa, Dartford.

Science Lecturer; Lecturer in Organic Chemistry and Mathematics, Technical Schools, Southend-on-Sea. Two years Teacher of Physics, Boulevard Science School, Hull. Bachelor of Science (London). Am desirous of keeping in touch with all branches of Chemical Science.

Alf. J. Parker. Jas. Baynes.
F. W. De Velling, Thomas Luxton.
W. H. Templeman.

Marsh, John,

29 High St., Maidstone.

Assistant Chemist to the Associated Portland Cement Manufacturers, Ltd. I have taken the 3 years' Diploma Course in Chemistry at the Central Technical College, Exhibition Rd., S.W.

Henry E. Armstrong. T. M. Lowry.
Gerald T. Moody. William A. Davis.
Edward W. Lewis.

Mellor, Joseph William,

62 Bland Street, Moss Side, Manchester.

Doctor of Science, (N.Z. University); First Class Honours (chemistry); 3 years 1851 Exhibition Scholar; late Senior Scholar (N.Z. University); engaged in Research work, as Research Fellow, at the Owens College from 1899 up to present time; published papers in *Transactions Chemical Society* "On Union of H and Cl," &c.; and papers in other Scientific Journals. Author of "Higher Mathematics for Students of Chemistry," &c. (Longmans, Green and Co., London).

H. B. Dixon. W. H. Perkin, jun.
J. F. Thorpe. Francis V. Darbishire.
R. S. Hutton.

Millington, John Price,

Christ's College, Cambridge.

Student. Junior Demonstrator in the Camb. University Chemical Laboratory, Scholar of Christ's College, Cambridge. First Class in Natural Sciences Tripos Part I., B.A. (Camb.), B.Sc. (Wales).

G. D. Liveing. H. J. H. Fenton.
W. J. Sell. H. O. Jones.
T. B. Wood.

Phelps, John,

Trinity College, Oxford.

Student of Chemistry. B.A. (Oxon), Millard Scholar, Trinity College, Oxford. Honours in Chemistry, 1st Class, Natural Science Final Schools, Oxford 1902.

H. Brereton Baker. Arthur J. Webb.
D. H. Nagel. J. E. Marsh.
Henry A. Miers. N. V. Sidgwick.

Ricketts, Guy Dunstan,

Sir John Cass Technical Institute, Jewry Street, E.C.

Lecturer on Metallurgy at the above Institute. M.A. (Cantab.), Natural Sciences Tripos, Part I., 1898; Associateship Examination in Metallurgy, Royal School of Mines, 1900; Assistant in Sir W. C. Roberts-Austen's Research Laboratory, 1901.

W. C. Roberts-Austen. Charles T. Heycock.
T. K. Rose. Charles A. Kohn.
W. H. Merrett.

Ross, George Archibald Park,

20, Westhall Gardens, Edinburgh.

Medical Practitioner (M.B., Ch.B. Edin.). Graduated M.B. Ch.B. at Edinburgh in 1901. D.P.H. of the Royal Colleges Edin. in 1902. Intend taking up Public Health work in the Colonies and am desirous of keeping in touch with Chemical progress.

G. H. Gemmell. J. Falconer King.
Hugh Marshall. Alex Crum Brown.
William C. Ross. Thos. Darling.
Leonard Dobbin.

Sampson, John William,

Helpringham, Heckington, Lincs.

Analytical Chemist. For two years engaged in Organic and Analytical Chemistry under Mr. F. Bedford, B.Sc. (Lond.). For some

time demonstrator in Practical Chemistry at Metropolitan College of Pharmacy. Have passed Major Exam. of Pharmaceutical Society. Desirous of increasing my knowledge of Chemistry.

F. Stanley Kipping. R. M. Caven.
G. Druce Lander. Fred Bedford.
W. Watson Will. Harry Lucas.
F. Filmer De Morgan.

Sindall, Robert Walter,

80, Manor Rd., Brockley, London, S.E.

Analyst, Chemical Engineer, Paper Trade Expert. Student under Professor Armstrong at the City and Guilds Institute, South Kensington. For some years Analyst and Chemical Engineer to Messrs. Edward Lloyd, Ltd. Papermakers, England, Norway, Canada. Now Consulting Chemist and Expert to the Pulp and Paper Trades.

Henry E. Armstrong. W. Palmer Wynne.
H. F. C. Goltz. William J. Pope.
Stanley J. Peachey. Clayton Beadle.

Simpson, Duncan,

10, Brynmill Crescent, Swansea.

Assayer. Having had 18 months' study of Analytical Chemistry under the late W. Terrill, Esq.; 3 months' practice in the Cape Copper Co.'s Laboratory; 3 years at the Swansea Hæmatite Iron and Steel Works under F. B. Last, Esq.; 13 months in Emu Spelter Works, research and analytical work under Messrs. Sulman and Picard on their patent process for treatment of sulphide ores of lead and zinc, and having in connection with this last invented and protected a process for the treatment of the furnace residues, and having since been engaged at J. S. Merry and Co.'s Lab. in work on Au, Ag, Cu, and Pb ores, &c., and having during the whole of the last seven years attended South Kensington night classes in Chemistry, Metallurgy, and Physics, Hons. Certificate.

E. Howard Tripp. Godfrey Millard.
Christopher James. Frank B. Last.
L. Ludlow. *John W. Bevan.*
Clarence A. Seyler.

Smith, Leonard,

14, West Hill, Highgate, London, N.

Student of City and Guilds of London Central Technical College. I have been a student in the Chemical Department of the above College for three years and am now engaged in research.

Henry E. Armstrong. William A. Davis.
Gerald T. Moody. T. Martin Lowry.
Edward W. Lewis.

Smythe, John Seabury, B.Sc., Ph.D.,
143, Smithdown Lane, Liverpool.

Analytical Chemist. B.Sc. (Vict.) Honours Chemistry 1897; Ph.D. (Würzburg) 1899. Chemist with Messrs. W. Meadowcroft and Son, Ltd., Blackburn, Essence Distillers and Manufacturing Chemists, since January, 1900.

J. Campbell Brown. Herbert B. Stocks.
W. Collingwood Williams. *Prosper H. Marsden.*
F. H. Tate.

Stansfield, Edgar, B.Sc.,
Technical College, Sunderland.

Assistant Lecturer and Demonstrator in Chemistry, the Technical College, Sunderland. Student at Owens College 1897—1901, elected a Research Student October 1901. Obtained degree of B.Sc. (Vict.) Honours School of Chemistry, June 1900. Original Research: "Preliminary Note on the Preparation of Barium" read before the Manchester Lit. and Phil. Society October 29, 1901.

H. B. Dixon. J. F. Thorpe.
W. H. Perkin, jun. R. S. Hutton.
E. Clark.

Sutherst, Walter Frederick,
Cheshire Agricultural College, Holmes Chapel.

Lecturer in Chemistry and Analyst. Diploma of Federal Polytechnic, Zürich. Ph.D. (Geneva). A.I.C. Published following investigations: "The Solubility of Phosphatic Manures in some Organic Acids" (*Chem. News*, 2187); "the Freezing Point of Vegetable Saps and Juices" (*Chem. News*, 2190); "Influence of Manuring on Chemical Composition of Potatoes" (*Chem. News*, 2192); "Effect of Lime on the Insoluble Phosphates in Soils" (*Chem. News*, 2210); "the Composition of Colostrum" (*Chem. News*, 2223); "the Reversion of Superphosphate in Soils" (*Agricultural Gazette*, Sept. 1st, 1902); "Chemical Changes in the Ripening of Cheshire Cheese" (*Soc. Chem. Ind.*, Feb. 28th, 1902). Thesis: "Derivatives of Naphthazonium."

Edric Druce. Bernard Dyer.
J. Carter Bell. Walter M. Gardner
A. B. Knaggs.

Thomson, George Sutherland,
Government Offices, Adelaide, South Australia.

Scientific Dairy Expert to the Government of South Australia. Author of "Preservatives in Dairy Produce, with Analyses"; "Causes

of Variation in the Water Percentage of Butter (with analyses)"; "Cheese Experiments and Analyses"; "Cattle-feeding Experiments and Analyses," and "Stale Butter and Analyses," issued by the Government of South Australia. Instructor in Dairy Science at Government School of Mines; College of Agriculture; School of Agriculture; Agricultural Bureaus, and to the Dairy Factory Managers in South Australia.

Thomas S. Goodwin. James Hendrick.
J. F. Blackshaw. *Frederick J. Lloyd.*
C. M. Aikman. *James McCutcheon.*
Jas. McCreath.

Tidy, Henry Letheby,
New College, Oxford.
Medical Student. Graduate in Chemistry of Oxford University.

William Odling. James Dewar.
William Crookes. Harold Hartley.
D. H. Nagel.

Wallis, Thomas Edward,
78, Essex Road, Islington, N.
Assistant Lecturer in Chemistry in the School of Pharmacy of the Pharmaceutical Society. B.Sc. (Lond.). Have published several papers dealing with the anatomy of drugs; 1899 to 1900 Junior Demonstrator in Practical Chemistry; 1900 to 1901 Demonstrator in Pharmaceutics in the School of Pharmacy.

J. Norman Collie. M. Carteighe.
A. Lapworth. Walter Hills.
D. Northall-Laurie.

White, William Carter,
113, Gower Street, W.C.
Analyst to Messrs. Geo. Curling, Wyman & Co., 58, Bunhill Row, E.C. Joint author of "Removal of Fat from Nux Vomica Preparations," *C. & D.*, lxi., p. 87. Author of "Cobalt Nitrate as a Reagent." *Ph. J.*, 4th series, 1674, p. 68.

William Fowler. Peter MacEwan.
W. L. Howie. Thomas Tyrer.
A. K. Huntington.

Wilson, Lyndon,
66, Castle Gate, Newark-on-Trent.
Analytical Chemist to Messrs. J. Richardson & Son, Newark-on-

Trent. Analytical Chemistry under J. Heron, Esq. Practical and Scientific Brewer and Maltster.

John Heron.	Arthur R. Ling.
Leonard Temple Thorne.	*E. Haynes Jeffers.*
Wm. G. Johnstone.	*F. Jewson.*

The following Certificates were authorised by Council under Bye-law I. (3):

Edminson, Sidney Robert,
Maritzburg College, Natal.

Schoolmaster, B.Sc. (London) in Chemistry, &c., for some years a chemical student at Firth College, Sheffield. Teacher of Chemistry at Maritzburg College, Natal, S. Africa. For five years Science Master at Wesley College, Sheffield.

Percy John Vinter.

Mukergee, Beni Madhav,
Roorkee, India.

Science Demonstrator, Thomason College, Roorkee, India. Graduate (science course) of the Allahabad University, formerly Science Demonstrator for four years in the Muir Central College, Allahabad. Since 1899, Demonstrator in the Thomason College, Roorkee, in which capacity he has to lecture to the Engineer Classes on Chemistry and also do the commercial analysis undertaken by the College.

Abhayacharan Sanyal.

Přibram, Richard, Ph.D.
The University, Czernowitz, Austria.

Professor of Chemistry in the University of Czernowitz.

Hans Meyer. *William Ramsay.*

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 9/12/02

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 18. No. 257.

Thursday, December 4th, 1902. Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

Mr. J. H. Ryffel was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs.:

Cousins, Francis George, Queen's Road, London, N.
Elford, Archibald Sefton, B.A., 9, Keble Road, Oxford.
Huyin, Moung Tha, B.A., 18, Mercers Road, London, N.
Kemp-Welch, Maurice, Parkstone, Weybridge, Surrey.
Sibley, Samuel Edward, 3, Rutland Road, Ilford.
Turner, Duncan, Elmbank, Broomhouse, near Glasgow.

A ballot for the election of Fellows was held, when the following were declared duly elected :—

John Frederick Alder.
Alfred Edward Beanes.
Herbert Blair.
John A. H. Brincker, B.A., M.B.
Vernon Seymour Bryant, B.A.
Thomas Burnell Carmichael.
Charles Cockle.
James Justinian Drought.
Edgar Leeder Edlin, B.A.
Sidney Robert Edminson, B.Sc.
Walter Henry Edwards.
George Felix Dudbridge Green.
Wilfrid Russell Grimwade, B.Sc.,
Edward Gumersall.
David Vincent Hollingworth.
Alfred Holt, jun., B.A.
Arthur Francis Hosking.
Clements F. V. Jackson.
Douglas Kennedy Jardine, B.Sc.
John Petty Leather.
Frank Austin Lidbury, M.Sc.
Ernest Liotard.
Thomas Stratford Logan.
Douglas A. MacCallum.
William Mann, B.Sc.
John Marsh.
Joseph William Mellor, D.Sc.
John Price Millington, B.A., B.Sc.
Beni Madhav Mukerjee.
John Phelps, B.A.
Richard Přibram, Ph.D.
Guy Dunstan Ricketts, M.A.
George Archibald Park Ross, M.B.
John William Sampson.
Duncan Simpson.
Robert Walter Sindall.
Leonard Smith.
John Seabury Smythe, B.Sc., Ph.D.
Edgar Stansfield, B.Sc.
Walter F. Sutherst, Ph.D.
George Sutherland Thomson.
Henry Letheby Tidy, B.A.
Thomas Edward Wallis, B.Sc.
William Carter White.
Lyndon Wilson.

Of the following papers, those marked * were read :

*173. "The specific heats of liquids." By H. Crompton.

It is assumed that when heat is applied to a liquid, if there is no change in its molecular composition, (1) there is an increase in the kinetic energy of the molecules, (2) internal work is done within each molecule, (3) there is a diminution in the attraction of the molecules for one another, (4) some external work is done. The last quantity is neglected in considering the specific heat, and the first and second changes are taken to have the same effect on the specific heat of the liquid and on that of its vapour, so that together they make up the specific heat at constant volume of the vapour. At any absolute temperature T, the molecular heat at constant volume of the vapour $C_v = 2{\cdot}96 + 0{\cdot}000245 M v_b T \log n$, where n is the number of atoms in the molecule, and Mv_b is the molecular volume of the liquid at the boiling point. The molecular attraction is regarded as measured by the difference between the latent heat of condensation of the vapour and the heat evolved on simply compressing the vapour into the volume of the liquid without causing a change of

state. This attraction is assumed to become zero at the critical temperature and to increase regularly with the fall in temperature from the critical point downwards. At the absolute temperature T, the change in the attraction is therefore

$$dA/dT = (L - RT\log V_o/v_o)/(T_k - T),$$

in which L is the latent heat of condensation, R the constant of the gas equation, V_o and v_o the volumes of the vapour and liquid respectively, and T_k the absolute critical temperature. It follows from the above that the molecular heat of the liquid is $C_f = C_v + dA/dT$, and the author showed that the molecular heats of liquids thus calculated agree fairly with those observed, except where molecular association occurs in the liquid.

***174. "The constitution of enolic benzoylcamphor." By M. O. Forster.**

From the production of camphorquinone by oxidising benzoylcamphor with chromic acid and with mercuric acetate, it is concluded that the enolic modification of benzoylcamphor has the constitution of *phenylhydroxymethylenecamphor*, $C_8H_{14}\langle \begin{matrix} C{:}C(OH)\cdot C_6H_5 \\ CO \end{matrix}$.

Phenylchloromethylenecamphor, $C_8H_{14}\langle \begin{matrix} C{:}CCl\cdot C_6H_5 \\ CO \end{matrix}$, obtained from enolic benzoylcamphor and phosphorus pentachloride, melts at 100° and its rotation $[\alpha]_D = -217°$; the alcoholic solution gives no coloration with ferric chloride. Aniline converts it into *anilinophenylmethylenecamphor anil*, $C_{29}H_{30}N_2$, sulphur-yellow plates m. p. 117—118°; the *acetyl* derivative, $C_{31}H_{32}ON_2$, melts at 166°.

When phenylchloromethylenecamphor is heated with alcoholic ammonia in sealed tubes at 150—170°, a *base* having the formula $C_{17}H_{21}ON$ is produced. This melts at 170°, its rotation $[\alpha]_D = +180{\cdot}2°$; it gives an intense blue coloration with ethereal ferric chloride; the *picrate* melts at 157° and the *benzoyl* derivative at 99—100°.

On heating enolic benzoylcamphor with ammonium formate in sealed tubes at 200—220°, another *base*, also having the formula $C_{17}H_{21}ON$, is formed. It melts at 118—119°, its rotation $[\alpha]_D = +235{\cdot}2°$: it gives no colour with ferric chloride; it does not combine with benzaldehyde or benzoyl chloride, but yields a *picrate* which does not melt at 250°, and a *bromo*-derivative, $C_{17}H_{20}ONBr_5$, orange-red plates, m. p. 173°.

Enolic benzoylcamphor is reduced in alkaline solution by sodium amalgam, yielding benzylidenecamphor and benzylcamphor. Potassium permanganate oxidises it to a mixture of benzoic and camphoric acids,

whilst potassium ferricyanide gives rise to a *compound* having the formula $C_{34}H_{38}O_4$ and m. p. 221°, its rotation $[\alpha]_D = +270{\cdot}4°$; it does not react with ferric chloride, and is insoluble in alkalis.

***175. "Isomeric benzoyl derivatives from *iso*nitrosocamphor." By M. O. Forster.**

When *iso*nitrosocamphor is treated with benzoyl chloride in presence of sodium hydroxide, two compounds are produced each having the empirical formula $C_{17}H_{19}O_3N$.

The *compound* from which *iso*nitrosocamphor can be regenerated by hydrolysis, crystallises from alcohol in large, yellow prisms melting at 105—106°; it is readily soluble in petroleum, and its rotation $[\alpha]_D = +145{\cdot}6°$ in chloroform. The *iso*nitrosocamphor obtained from this derivative has the rotation $[\alpha]_D = +221{\cdot}9°$, and yields the two new substances on benzoylation.

The compound which accompanies the above-mentioned derivative, although isomeric with it, does not give rise to *iso*nitrosocamphor on hydrolysis; it is scarcely soluble in petroleum, and crystallises from alcohol in colourless, lustrous laminæ melting at 136° and its rotation $[\alpha]_D = +126{\cdot}9°$ in chloroform. Alcoholic potash resolves it into a mixture of benzoic and cyanolauronic (*a*-camphornitrilic) acids.

***176. "Action of phosphorus haloids on dihydroresorcins. Part I. Dimethyldihydroresorcin." By A. W. Crossley and H. R. Le Sueur.**

Phosphorus trichloride reacts with dimethyldihydroresorcin, giving *5-chloro-3-keto-1:1-dimethyl-*Δ^4*-tetrahydrobenzene*, $CMe_2<\begin{matrix}CH_2-CO\\CH_2\cdot CCl\end{matrix}>CH$, a colourless liquid boiling at 109° (14 mm.), and also small quantities of an *anhydride* of *dimethyldihydroresorcin*, $(C_8H_{11}O)_2O$, melting at 99·5°.

Phosphorus oxychloride gives the same chloroketone, and phosphorus tribromide the corresponding bromo-compound, $C_8H_{11}OBr$, which boils at 129° (25 mm.).

When phosphorus pentachloride acts on dimethyldihydroresorcin, 3:5-dichloro-1:1-dimethyl-$\Delta^{2:4}$-dihydrobenzene (*Trans.*, 1902, **81**, 826) and 3:5-dichloro-*o*-xylene (*Trans.*, 1902, **81**, 1533) are obtained.

By the action of phosphorus pentabromide on dimethyldihydroresorcin, bromodimethyldihydroresorcin is first formed, and the products of the action of the phosphorus bromides on this compound have been investigated. With phosphorus tribromide there is obtained a mixture of mono- and *di-bromoketodimethyltetrahydrobenzene*, the latter,

having the formula $C_8H_{10}OBr_2$, melts at 96°; and a liquid which on treatment with bromine is converted into a *tribromoxylenol* which melts at 176—177·5°. By the further action of bromine the above dibromoketone is converted into *tri-* and *tetra-bromoketodimethyltetrahydrobenzene*, which melt respectively at 106° and 118°. These latter substances are also produced by the action of phosphorus pentabromide on bromodimethyldihydroresorcin.

The action of phosphorus pentabromide on dimethyldihydroresorcin is one which is largely influenced by the conditions under which the experiments are carried out. The following products of the reaction have been isolated: bromodimethyldihydroresorcin, tribromoketotetrahydrobenzene, a *bromoxylenol*, C_8H_9OBr, melting at 83·5—84°, a *dibromoxylenol* melting at 96·5°, and two *tribromoxylenols* melting at 176—177·5° and 182—183° respectively.

177. "The absorption spectra of metallic nitrates. Part II." By W. N. Hartley, D.Sc., F.R.S.

The substances examined were aqueous solutions of the nitrates of fifteen metals, and of nitric, sulphuric, and hydrochloric acids, and alcoholic solutions of ethyl and lithium nitrates.

Metals which exhibit characteristic absorption bands show variations in the positions and intensities of these bands which appear to be dependent upon the molecular weights of the salts in solution. Equivalent quantities of certain metals exhibit the same absorption spectra whether in strong or dilute solution, and, in certain cases, through a great range in dilution. A dilute solution of silver nitrate transmits a longer range of spectrum than a strong solution containing the same quantity of salt. The effect of dilution on nitric acid of sp. gr. 1·42 is the reverse of that observed in the case of silver nitrate. There is a remarkable difference between the constitution of ethyl nitrate on the one hand (whether undiluted or in dilute alcoholic solution), and that of solutions equally dilute of inorganic nitrates on the other. The effect of raising the temperature of the solutions is simply to intensify the absorption spectrum as if a stronger solution at a lower temperature had been used.

Although evidence of what may be regarded as ionic dissociation is afforded by the spectra of dilute solutions of the inorganic nitrates, yet the spectra themselves are not alike, as they would be if the salts were completely resolved into NO_3 and metallic ions; the evidence is just as favourable to the view that some of the salts are resolved into nitric acid and the corresponding base.

In the case of esters, like ethyl nitrate, the conditions are entirely

different, as the molecule is clearly not dissociated, there being no evidence of the $-NO_3$ group in the compound.

Views in explanation of the facts observed were put forward.

178. "The constitution of the products of nitration of meta-acetoluidide." By J. B. Cohen and H. D. Dakin.

The authors show that the nitro-derivative of *m*-acetoluidide obtained by Beilstein and Kuhlberg (*Annalen*, 1871, **158**, 348) contains the nitro-group in the para-position with respect to the amido-group, and not in the ortho-position as stated by Limpricht (*Ber.*, 1885, **18**, 403). The substance was successively converted into 3-chloro-6-nitrotoluene and 3-chloro-4 : 6-dinitrotoluene.

By fractional crystallisation from alcohol of the products of nitration, a nitro-derivative which had hitherto escaped observation was separated, which proved to be 4-nitro-3-acetylaminotoluene. On hydrolysis it gave a base identical with the 4-nitro-3-aminotoluene obtained by Staedel and Kolb (*Annalen*, 1890, **259**, 224) by the action of ammonia on 4-nitro-*m*-cresol ethyl ether.

179. "The action of metallic thiocyanates upon carbonyl chloride." By A. E. Dixon.

When carbonyl chloride dissolved in toluene is allowed to stand in contact with excess of finely divided sodium, potassium, barium, mercury, or lead thiocyanate, interaction gradually occurs with formation of metallic chloride, and a substance possessing the general chemical characters of a thiocarbimide, but giving, under certain conditions, the reactions of a thiocyanate. It has recently been pointed out by the author that tautomerism of this kind often occurs among the so-called "thiocyanates" of electro-negative radicles (*Trans.*, 1901, **79**, 541). The interaction may be represented thus: $COCl_2 + Pb(SCN)_2 = PbCl_2 + CO(NCS)_2$, but it does not take place quantitatively, *iso*persulphocyanic acid and *pseudo*-sulphocyanogen and occasionally other products being formed. Heating to about 100° greatly accelerates the change, but even after thirty hours not more than one-third of the carbonyl chloride employed is converted into thiocarbimide, and much remains unchanged.

Hitherto, all attempts to isolate carbonyldithiocarbimide in a pure state have failed, but its solution interacts with alcohol and with nitrogenous bases, yielding additive products.

Only one molecule of ethyl alcohol could be caused to unite with one of dithiocarbimide; the resultant *hemi*-thiourethane,

$$SCN\cdot CO\cdot NH\cdot CS\cdot OEt,$$

was obtained in pale yellow prisms melting at 141—142°. It is insoluble in cold water, but decomposes when heated with water to near the boiling point, carbon dioxide and thiocyanic acid being formed.

By combination with aniline, compounds having either the formula SCN·CO·NH·CS·NHPh or $CO(NH·CS·NHPh)_2$, can be obtained, according to the conditions. The former, *carbonylthiocarbimidophenylthiocarbamide*, crystallises from alcohol in brilliant, pearly leaflets which melt at 172°, then quickly resolidify, and now melt at 223°. It is insoluble in cold water, but gradually dissolves on boiling, becoming hydrolysed, carbon dioxide being evolved, whilst thiocyanic acid and phenylthiourea remain dissolved: $SCN·CO·NH·CS·NHPh + H_2O = CO_2 + HSCN + CSN_2H_3Ph$.

Carbonyldiphenyldithiocarbamide, $CO(NH·CS·NHPh)_2$, separates from alcohol in vitreous prisms which melt at 166° and are insoluble in boiling water. Both phenylated derivatives, as well as the *hemi*-thiourethane, are readily desulphurised by silver salts and by an alkaline lead solution.

Attempts to produce *hemi*- or complete thiourethanes by adding carbonyl chloride to potassium or barium thiocyanate in alcoholic solution were unsuccessful; the chloride first interacted with the alcohol, yielding ethyl chlorocarbonate, which, with the metallic thiocyanate, gave carboxyethylthiocarbimide, and this latter, combining with another portion of the alcohol, formed finally Doran's carboxyethylthiourethane (*Trans.*, 1896, **69**, 334) or diethyl iminothiodicarbonate, EtO·CO·NH·CS·OEt.

The following compounds were also described:

Carbonylthiocarbimidoparatolylthiocarbamide,

$$SCN·CO·NH·CS·NH·C_7H_7.$$

—Pearly leaflets melting at 182°, resolidifying at once, and now melting at 237°. In general properties, this and the naphthyl compound mentioned below closely resemble the phenyl homologue. *Carbonyldi-o-tolyldithiocarbamide*, $CO(NH·CS·NH·C_7H_7)_2$.—M. p. 172° has properties similar to those of the corresponding diphenyl compound. *Carbonylthiocarbimido-α-naphthylthiocarbamide*,

$$SCN·CO·NH·CS·NH·C_{10}H_7,$$

is a yellowish powder, m. p. 182°, resolidifying at once and then melting at 222°.

Carbonylthiocarbimidophenylbenzylthiocarbamide,

$$SCN·CO·NH·CS·NPhBz.$$

—Prepared from benzylaniline, it formed long, vitreous prisms having a faint yellow tinge, and melting with effervescence at 180°. When boiled with water it slowly undergoes hydrolysis, carbonic anhydride being evolved, thiocyanic acid passing into solution, and αα-phenylbenzylthiourea, $NH_2·CS·NPhBz$, being left.

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At the next ordinary meeting, on **Wednesday**, December 17th, at 5.30 p.m., the following papers will be communicated.

"A reagent for the detection of carbamide and of certain other nitrogen compounds." By H. J. H. Fenton.

"The rate of decomposition of diazo-compounds. Part II. Diazo-compounds of the naphthalene series." By J. C. Cain and F. Nicoll.

"The state of carbon dioxide in aqueous solution." By J. Walker.

"The qualitative separation of arsenic, antimony and tin." By J. Walker.

"The hydrates and the solubility of barium acetate." By J. Walker and W. A. Fyffe.

"*cis*- and *trans*-$\alpha\beta$-Dimethylglutaric acid and the separation of the *cis*- and *trans*-forms of substituted glutaric acids." By J. F. Thorpe and W. J. Young.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY

Issued 2/1/03

PROCEEDINGS

OF THE

CHEMICAL SOCIETY

EDITED BY THE SECRETARY

Vol. 18. No. 258.

Wednesday, December 17th, 1902. Professor J. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs.:

Edwin Bayles Atkinson, Scarthe House, Great Grimsby.
William Bowen, Cleveden, Woodend Road, Erdington.
R. C. Farmer, M.Sc., Ph.D., 154, Eglinton Road, Woolwich, S.E.
Frederic Herbert Lees, 256, Park Road, Crouch End, N.
A. H. Scholefield, B.A., B.Sc., 4, Hartley Terrace, Wolverhampton.
Charles Tilburn, 31, Hardy Street, South Yarra, Melbourne.
Andrew Young, M.A., B.Sc., 1, Avenue Terrace, Cape Town.

The following Certificates were authorised by the Council under Bye-law I. (3):

K. Bhaduri, M.A., Professor, Canning College, Lucknow.
George Montague Prichard, Ramtek, Nagpur, C.P., India.

Of the following papers, those marked * were read:

*180. "A reagent for the identification of carbamide and of certain other nitrogen compounds." By H. J. H. Fenton.

In previous communications to the Society (Fenton and Gostling, *Trans.*, 1899, 77, 423; 1901, 81, 807), various derivatives of methyl-

furfural have been described which are obtained from ketohexoses, or substances which produce these on hydrolysis, and from cellulose. Amongst these derivatives, a crystalline condensation product was mentioned having the formula $C_{11}H_8O_4$, the constitution of which is still under investigation; the evidence obtained so far indicates that it is either methyl-furil, $C_4H_3O{\cdot}CO{\cdot}CO{\cdot}C_4H_2O{\cdot}CH_3$, or the ketone-aldehyde, $CHO{\cdot}C_4H_2O{\cdot}CO{\cdot}C_4H_2O{\cdot}CH_3$. The method of obtaining this substance has been considerably improved, so that it is now easy to prepare it in quantity. If a small quantity of this product be mixed with urea and the mixture treated with a trace of phosphorus oxychloride, acetyl chloride or dry hydrogen chloride—dissolved in any appropriate solvent—a very brilliant blue colour is obtained. The reaction is one of extreme delicacy, 0·1 milligram of urea giving a strongly marked colour, and with care it is quite easy to detect 0·01 milligram or less.

This effect is due to a colourless base of which the salts have a blue colour. The intensity of the colour of these salts in aqueous solution varies markedly with the nature and concentration of the acid.

The production of a blue colour in the manner here described is characteristic of carbamide and of mono-substituted carbamides, $NH_2{\cdot}CO{\cdot}NHR$, in which the substituting radicle is an alkyl group or one of a similar character; acidyl substituted carbamides give no such reaction. Urethane gives a similar reaction, but the colour is red by transmitted light.

This compound also reacts with primary amines in acetic acid solution to give very brilliant green compounds; this change is produced at once on simply mixing the solutions without any condensing agent, and appears to be quite characteristic of primary amines.

Discussion.

Mr. C. E. Groves asked whether oxalic acid behaved like sulphuric and hydrochloric acids.

Mr. Fenton replied that the base gave a blue colour with oxalic acid also, the intensity of the colour being greater than that produced with acetic acid, but less than that with hydrochloric acid.

***181. "The rate of decomposition of diazo-compounds. Part II. Diazo-compounds of the naphthalene series." By J. C. Cain and F. Nicoll.**

The authors have extended their researches on the decomposition of diazo-salts (*Trans.*, 1902, 81, 1412) to those of the naphthalene series, and find that the reaction is a unimolecular one in the case of the soluble diazo-salts prepared from the following amines:

1. α-Naphthylamine.
2. β-Naphthylamine.
3. Naphthylaminesulphonic acid, $NH_2 : SO_3H = 1 : 8$.
4. „ „ „ $= 2 : 6$.
5. „ „ „ $= 2 : 7$.
6. „ disulphonic acid, $NH_2 : SO_3H : SO_3H = 2 : 6 : 8$.
7. „ „ „ $= 2 : 3 : 6$.
8. Amidonaphtholdisulphonic acid, $NH_2 : OH : SO_3H : SO_3H = 1 : 8 : 3 : 6$.

The unimolecular reaction, however, in the case of Nos. 1, 2, 4, 5, 7, 8, is hindered, after a considerable amount of decomposition has taken place, by the formation of azo-colours, which is clearly shown by the rapid diminution of the values of C, calculated according to the equation $\frac{1}{t}\log\frac{A}{A-x} = C$ (a constant).

The measurements were made at 60°, except in the case of No. 8, when the temperature was 80°. The diazo-salts are thus very stable.

In the case of the insoluble diazo-salts obtained from the following amines:

9. Naphthylaminesulphonic acid, $NH_2 : SO_3H = 1 : 2$.
10. „ „ „ $= 1 : 4$.
11. „ „ „ $= 1 : 5$.
12. Amidonaphtholsulphonic acid, $NH_2 : OH : SO_3H = 2 : 8 : 6$.

the rate of decomposition is expressed by the equation $\frac{x}{t} = K$ (a constant), x being the observed volume of nitrogen evolved in the time t.

In each case, an azo-colour is formed towards the end of the reaction, shown again by the rapid diminution of the values of K.

These diazo-salts are very stable, the experiments being made at 70° or 80°.

In each case where an azo-colour is formed, the value of C or K is constant for a considerable period, showing that, although both naphtholsulphonic acid and diazo-salt are present, no combination takes place during this period.

The authors suggest that this interesting fact may be explained by assuming that hydrolytic dissociation of the diazo-salt is necessary before combination takes place; in the above experiments, the diazo-salt is not dissociated (especially in the presence of the free mineral acid, which has a retarding effect on the formation of an azo-colour) until its concentration becomes considerably less. When this point is reached, the formation of an azo-colour can proceed.

*182. "State of carbon dioxide in aqueous solution." By J. Walker.

The author gave a proof from the law of mass-action that carbonic acid (and similar substances) in aqueous solution must obey Ostwald's dilution law, independently of the proportions of the anhydrous and hydrated forms contained in the solution. The conclusion formerly drawn (Walker and Cormack, *Trans.*, 1900, 77, 8), that the carbon dioxide in solution is probably hydrated to the extent of 20 per cent., must therefore be rejected.

*183. "Qualitative separation of arsenic, antimony, and tin." By J. Walker.

When a solution of the sodium thio-salts of arsenic, antimony, and tin is boiled with sodium peroxide, these salts are converted into sodium arsenate, antimonate, and stannate respectively. Any mercury which may have been dissolved from the copper group on warming with sodium hydroxide, is, by this treatment, reprecipitated as sulphide. The tin may be separated from the arsenic and antimony by boiling with excess of ammonium chloride, which precipitates stannic hydroxide, leaving the antimony and arsenic in solution. On addition of excess of acid, these may be separated by means of sulphuretted hydrogen in the cold, the antimony being at once precipitated as sulphide, whilst the arsenic remains dissolved.

Discussion.

Dr. F. M. Perkin remarked that when stannous sulphide does not dissolve in caustic alkali, the addition of a little sodium or hydrogen peroxide enables it to do so. The peroxide seems to exert very little, if any, oxidising action upon the sulphides of the copper group, hence there is no objection to warming the mixed sulphides of these two groups with caustic alkali and sodium peroxide and so obviating the use of ammonium sulphide.

*184. "The hydrates and solubility of barium acetate." By J. Walker and W. A. Fyffe.

The authors have been unable to confirm the observations of Krasnicki (*Monatshefte*, 1887, 8, 601), who stated that the solubility of barium acetate between 0° and 80° could be represented by a single curve concave to the temperature axis. On the contrary, they find that the solubility is expressed by three curves (for the trihydrate, mono-

hydrate, and anhydrous salt, respectively), which are all convex to the temperature axis. The curve for the monohydrate exhibits a minimum at 30°, and that for the anhydrous salt a minimum at 75°.

The solubility and special dilatometric experiments showed the inversion temperature for $Ba(C_2H_3O_2)_2,3H_2O \rightleftharpoons Ba(C_2H_3O_2)_2,H_2O + 2H_2O$ to be 24·7°; that for $Ba(C_2H_3O_2)_2,H_2O \rightleftharpoons Ba(C_2H_3O_2)_2 + H_2O$ being 41°.

Discussion.

Professor Tilden expressed the belief that revision of many of the accepted data in regard to solubility was urgently required and hoped that Professor Walker would continue his work in this direction. Published estimations of solubility of many metallic salts at temperatures above the boiling point of water were absolutely valueless, inasmuch as evident chemical change sets in and basic salts are visibly deposited.

***185. "*cis*- and *trans*-$\alpha\beta$-Dimethylglutaric acid and the separation of the *cis*- and *trans*-forms of substituted glutaric acids." By J. F. Thorpe and W. J. Young.**

The $\alpha\beta$-dimethylglutaric acids are best prepared by the condensation of ethyl β-methylacrylate with ethyl sodiocyanacetate and subsequent treatment of the sodium derivative formed with methyl iodide.

Ethyl α-cyano-αβ-dimethylglutarate,

$$CO_2Et\cdot C(CN)(CH_3)\cdot CH(CH_3)\cdot CH_2\cdot CO_2Et,$$

is a colourless oil which boils at 185° (20 mm.), which, with cold methyl alcoholic potash, yields the *potassium* salt. *α-cyano-αβ-Dimethylglutaric acid* is a white solid which separates from ether and light petroleum in microscopic needles melting at 132—133°.

When this substance is heated with concentrated hydrochloric acid, it is in part converted into *αβ-dimethylglutarimide*, $CH_2\cdot CH<\begin{matrix}CH(CH_3)\cdot CO\\ CH_2\text{——}CO\end{matrix}>NH$, which crystallises from water in long needles melting at 113°, and in part into trans-*αβ-dimethylglutaric acid*, which appears to be a liquid at the ordinary temperature.

The imide, on hydrolysis with sulphuric acid, yields cis-*αβ-dimethylglutaric acid*, which crystallises from concentrated hydrochloric acid in needles melting at 87°.

The *trans*-acid is unacted upon by acetyl chloride, but when boiled with acetic anhydride or when slowly distilled under atmospheric pressure it is converted into the *anhydride* of the *cis*-acid, which may also be prepared by the action of acetyl chloride on the *cis*-acid. It is a liquid boiling at 255° (765 mm.). The *anilic acid* separates from dilute

alcohol in lustrous plates melting at 149°. The *cis*-acid, on heating in a sealed tube with concentrated hydrochloric acid, is converted into a mixture of the *cis*- and *trans*-acids.

The authors described the preparation of *αβ-dimethylpropanetricarboxylic acid*, $(CO_2H)_2{:}C(CH_3)\cdot CH(CH_3)\cdot CH_2\cdot CO_2H$, which crystallises from dilute hydrochloric acid in white needles melting with evolution of carbon dioxide at 165°. When heated to 200°, this acid is converted into a mixture of *cis*- and *trans*-*αβ*-dimethylglutaric acids.

The *cis*- and *trans*-forms of substituted glutaric acids may be separated by converting the mixed acids into their ammonium salts and heating them in a sealed tube at 160° for 4 hours. In this way, the ammonium salt of the *cis*-acid is converted into the imide, which, on hydrolysis with sulphuric acid, yields the *cis*-acid, whilst the *trans*-ammonium salt remains unchanged. The imide and ammonium salt are separated by means of ether.

The separation of *cis*- and *trans*-*aa'*-dimethylglutaric acids, of *cis*- and *trans*-*a*-methyl-*β*-*iso*propylglutaric acid, and of *cis*- and *trans*-*aa'ββ*-tetramethylglutaric acids have been thus effected.

***186. "Constitution of metallic cyanides." By J. E. Marsh.**

Volhard (*Annalen*, 1890, 259, 378) has shown that potassium cyanide is oxidised by potassium permanganate to potassium cyanate. Other cyanides are similarly oxidised. Ammonium cyanide is thus converted directly into urea. There are two exceptions among metallic cyanides; silver and mercury cyanides are not oxidised by potassium permanganate. This reaction brings the cyanides of silver and mercury into relationship with the nitriles, which are also unattacked. On the other hand, the other cyanides are brought into association with the readily oxidisable carbamines. The author thinks that silver cyanide should be represented as $Ag\cdot C{:}N$, and potassium cyanide as $K\cdot N{:}C$.

Discussion.

Dr. Wade said he thought it was unsafe to infer a difference in the constitution of potassium and silver cyanides from the difference in behaviour of these salts towards oxidising agents. The potassium salt is freely ionised in aqueous solution, whilst the silver salt is insoluble and not appreciably ionisable; the stability of the latter towards oxidising agents is thus explained without having recourse to the hypothesis of a nitrilic constitution. Potassium cyanide resembles the alkyl *iso*cyanides in readily undergoing oxidation, as in most other respects (*Trans.*, 1902, 81, 1606), but its ready ionisability in this

case destroys the parallel; the products of the oxidation of the undissociated alkyl *iso*-cyanides are complex and not comparable with the alkali cyanates, which are formed by the oxidation of *iso*-cyanogen ions.

***187. "Auto-reduction of mercury and silver cyanides." By J. E. Marsh and R. de J. F. Struthers.**

On the hypothesis that silver and mercury cyanides have the nitrile constitution, attempts have been made to bring about the hydrolysis of the (CN) group, if possible without breaking off the metal. In all the reactions tried in which the (CN) group is hydrolysed, it is broken off from the metal.

When mercuric cyanide is heated with a strong solution of potassium hydroxide, the salt is reduced to metallic mercury. The same reduction is brought about by boiling the salt with a solution of sodium or potassium hydroxide or ethylate in excess of alcohol. Cyanide and cyanate of the alkali are formed. The alkali cyanide formed protects the mercury salt from reduction, so that only half of the mercury is reduced. If potassium cyanide be previously mixed with the mercury salt, no reduction occurs. An intermediate product is being further investigated. Silver cyanide is also reduced in the same way.

When mercury cyanide is heated with from sixty to eighty times its weight of a mixture of equal volumes of sulphuric acid and water, hydrogen cyanide and carbon dioxide are evolved at about 130° and the whole mass sets to a jelly, from which mercurous sulphate is obtained on filtration; ammonium sulphate is also formed. The decomposition of the cyanide may be represented thus: $2HgC_2N_2 + 2H_2O + H_2SO_4 = Hg_2SO_4 + 3HCN + CO_2 + NH_3$. The decomposition of the cyanide is, however, not complete, and if the temperature is allowed to rise above 140°, whether the precipitate is previously removed or not, a further reduction takes place, with separation of metallic mercury. If mercury cyanide is heated with water in a sealed tube, the salt is completely decomposed, giving mercury, carbon monoxide, and ammonium carbonate. The reaction begins below 230° and may be thus expressed $HgC_2N_2 + 4H_2O = Hg + CO + (NH_4)_2CO_3$. No oxalic acid was obtained, but it was found that ammonium oxalate, under the same conditions, breaks up into carbon monoxide and ammonium carbonate. Silver cyanide is also reduced to metallic silver when heated with water.

188. "Note on the action of acids on cellulose." By Miss M. Gostling, B.Sc.

In previous communications it has been shown that all forms of cellulose, when heated to about 80° with a saturated solution of hydrochloric or hydrobromic acid in chloroform or carbon tetrachloride, yield ω-chlorobromomethylfurfural, and that dextrose (which could be extracted with water after separation of the methyl furfural derivative) was formed at the same time. Hence the presence of a ketose as well as an aldose nucleus in cellulose was conclusively proved.

In every case, about 40 per cent. of a black residue which retained the fibrous structure of the original cellulose was left after the action of the acids.

In the hope of throwing further light on the constitution of cellulose, the nature of this residue was investigated, and it was prepared free from any of the original cellulose by repeated treatment with hydrochloric acid until no more of the furfural derivative was formed.

Chlorine acted very slowly on this black residue, giving yellow derivatives containing from 25·7 to 34·35 per cent. of chlorine.

The action of bromine was similar.

Nitric acid (sp. gr. 1·2) and alkaline permanganate oxidise it to oxalic acid.

The original black residue is quite insoluble in alkalis, water, alcohol, ether, and other organic solvents.

The composition and general character of this residue is therefore closely allied to the substances known as artificial humus, obtained by Conrad and Guthzeit and by Sestini by the action of dilute acids on sugars. It corresponds most nearly with sacculmin (prepared by Sestini by boiling cane sugar with dilute sulphuric acid), which was a black, amorphous mass, insoluble in potash solution, giving, with chlorine, yellow chlorine compounds. Sestini gives to sacculmin the formula $C_{44}H_{38}O_{15}$ (C = 65·5; H = 4·8 per cent.), a slightly higher percentage of carbon and hydrogen than that in the black residue from cellulose (found C = 62·31 to 62·70; H = 3·64 to 4·29).

189. "Nitrotartaric acid and some of its ethereal salts." By P. F. Frankland, H. L. Heathcote, B.Sc., and Miss H. Hartle, B.Sc.

The announcement in the current number (Dec. 6th) of the *Berichte* that a paper is to be communicated to the Berlin Society on Dec. 8th by Professor P. Walden on the nitromalic and nitrotartaric esters,

compels the authors to publish without delay the results of work on which they have been engaged during the past four years.

Their investigation has included the preparation and characterisation of the following compounds: dinitrotartaric acid, dimethyl dinitrotartrate, diethyl dinitrotartrate, dimethyl mononitrotartrate, and diethyl mononitrotartrate. Of these, dinitrotartaric acid was first obtained by Reinsch (*Jahrb.*, 1849, 329) and Dessaignes (*Jahrb.*, 1852, 475), whilst Henry (*Ber.*, 1870, 3, 530) professes to have prepared diethyl dinitrotartrate; the other compounds are, as far as the authors are aware, described for the first time. The only reference to the optical properties which they have been able to discover in chemical literature is the statement by Dessaignes that Chautard had found dinitrotartaric acid to be optically active and dinitroracemic acid inactive. With regard to diethyl dinitrotartrate, the authors are of opinion that Henry must have been dealing with the mononitrotartrate, inasmuch as he gives no analysis, and the melting point 45—46°, which he records is very different from that which the authors have found, 27°, for the dinitro-, but very similar to that, 47°, which they have found for the mononitro-compound.

The authors have determined the optical activity of all these compounds dissolved in methyl and in ethyl alcohol, and, except in the case of dinitrotartaric acid, in benzene also.

The influence on the optical activity of the introduction of the nitro-group into the molecules concerned was also discussed.

190. "The nitration of diethyl monobenzoyl- and mono-*p*-toluyltartrates." By P. F. Frankland, H. L. Heathcote, B.Sc., and C. J. Green, M.Sc.

For the reasons given in the preceding abstract, the authors wish to communicate the results which they have obtained in this investigation, which was also commenced four years ago.

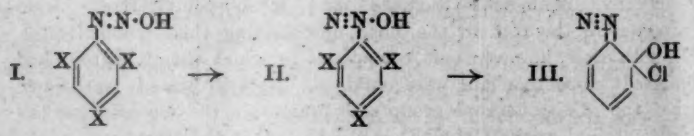
Diethyl mono-benzoyltartrate and mono-*p*-toluyltartrate were nitrated in the cold in the hope of obtaining their mono-nitrates. In both cases, however, only compounds in which the nitro-group had entered the benzene ring were obtained. By hydrolysis it was shown that the *m*-nitrobenzoyl group was present in the one case, and the nitro-*p*-toluyl group ($CH_3 : NO_2 : CO - 1 : 2 : 4$) in the other.

The rotation of these compounds was determined in solution in ethyl alcohol, ethyl acetate, benzene, pyridine, and chloroform. Their optical activity was enormously influenced by the solvent, thus the mono-*m*-nitrobenzoyl compound was inactive in benzene, although it exhibited considerable activity in the other solvents employed.

191. "Interchange of halogen for hydroxyl in chloro- and bromo-naphthalenediazonium hydroxides. Preliminary notice." By K. J. P. Orton.

It has recently been shown by the author that *s*-trichloro- and *s*-tribromo-benzenediazonium compounds undergo a remarkable isomeric change under certain conditions. If aqueous solutions of such salts as the diazonium nitrate or hydrogen sulphate are kept for a short time, the presence of chloride may soon be recognised by means of silver nitrate; at the same time, the solution becomes yellow, owing to the formation of the *o*-diazophenol (*o*-diazoquinone) The salts of a weak acid, such as the acetate, undergo the same change far more rapidly.

These facts lead to the conclusion that this change is a transformation of the diazonium hydroxide, $C_6H_2X_3{\cdot}N(OH){:}N$, formed by hydrolytic dissociation; the weaker the acid, the larger would be the proportion of the diazonium hydroxide present at any one time, and consequently the more rapid the change. Moreover, the presence of a sufficient excess of acid stops the change. Treatment with excess of alkali (hydroxide or carbonate), on the other hand, does not effect the elimination of halogen, but merely converts the diazonium compound, $C_6H_2X_3{\cdot}N(A){:}N$, into the diazotate (*iso-* or *anti*-diazotate), $C_6H_2X_3{\cdot}N{:}N{\cdot}OM'$. If dilute acid is cautiously added to a solution of the diazotate, halogen is also eliminated. On treatment with acid, the alkali diazotate should first of all yield the corresponding acid, the diazohydrate, $C_6H_2X_3{\cdot}N{:}N{\cdot}OH$, but, as is well known, these acids appear to change immediately into neutral substances, probably primary nitrosoamines. In the reaction here described, it would seem that the diazo-hydrate (I) is either transformed into the diazonium hydroxide (II) (or its ions), and then into a complex (III) of the quinone type, or else directly into this complex; from this quinonoid



compound, hydrogen chloride (or bromide) is eliminated, and a diazoquinone produced, or the halogen wanders to the nitrogen, a phenol diazonium salt being formed.

As the tendency to pass into the quinone type seems to be greater in the naphthalene series than in the benzene series, it would be expected that this transformation would take place with greater readiness

in the case of naphthalenediazonium compounds. Meldola and Streatfeild (*Trans.*, 1895, **67**, 908), who first observed this type of replacement of bromine by hydroxyl, have obtained 4-bromo-2-diazo-1-naphthol by treatment of 1 : 4-dibromo-2-naphthylamine, dissolved in acetic acid, with sodium nitrite, and subsequent boiling of the mixture with water. The author has studied the transformation of chloro- and bromo-naphthalenediazonium hydroxides, the solid salts of which have not hitherto been prepared.

1-*Chloro*-2-*naphthalenediazonium hydrogen sulphate*, $C_{10}H_6Cl\cdot N(SO_4H)\vdots N$, prepared from 1-chloro-2-naphthylamine, can be obtained (but with considerable difficulty) in the form of colourless needles, very soluble in water and acetic acid and moderately so in methyl alcohol. Exposed to the air, the crystals become yellow in a few minutes. The aqueous solution of the hydrogen sulphate, which is of course strongly acid, very rapidly becomes yellow and turbid. In the presence of sodium acetate, the change was complete in a few hours, and 2-diazo-1-naphthol (2-diazo-1-naphthoquinone), $O:C_{10}H_6:N_2$, had separated in long, slender, golden-yellow needles (m. p. 76—77°); at the same time, a small quantity of an amorphous, yellow solid containing chlorine was formed; it is probably an azo-condensation product. The chloride formed in the solution fell but little short of that contained in the diazonium salt. On passing dry hydrogen chloride into an ethereal solution of the diazonaphthol, a nearly colourless, crystalline *hydrochloride* is obtained.

2 : 4-*Dibromo*-1-*naphthalenediazonium hydrogen sulphate*,

$$C_{10}H_5Br_2\cdot N(SO_4H)\vdots N,$$

crystallises in colourless needles which are considerably more stable than the β-naphthalene derivative just described (compare Knoevenagel, *Ber.*, 1895, **28**, 2052). The aqueous solution of this salt rapidly becomes yellow, and after a short time begins to deposit the diazonaphthol in small rosettes of needles. In the presence of sodium acetate, the diazonium salt is completely decomposed in 24 hours, one atomic proportion of bromine being found in the solution. 4-*Bromo*-1-*diazo*-2-*naphthol* (4-*bromo*-1-*diazo*-2-*naphthoquinone*), $O:C_{10}H_5Br:N_2$, crystallises from dilute alcohol in rosettes of bright yellow needles, which melt and decompose with evolution of gas at 132—133°; it yields a nearly colourless *hydrochloride*.

192. "Purpurogallin." By A. G. Perkin and A. B. Steven.

The discovery of Nietzki and Steinmann (*Ber.*, 1887, **20**, 1277) that purpurogallin, on distillation with zinc dust, yields naphthalene has been confirmed. On methylation, purpurogallin gives a *trimethyl ether*,

$C_{11}H_5O_2(OCH_3)_3$, orange-yellow needles, m. p. 174—177°, which forms a *monoacetyl* derivative, $C_{11}H_4O_2(OCH_3)_3 \cdot C_2H_3O$, needles, m. p. 140—143°, and by the action of alcoholic potash at 170° yields a crystalline acid, m. p. 197—199°. The latter, on distillation, is converted into an anhydride, m. p. 164—166°. By digestion with 50 per cent. potassium hydroxide solution, purpurogallin is converted into two isomeric compounds possessing almost identical reactions, to which the names *purpurogallone* and *isopurpurogallone* have been given. The former, minute yellow needles, m. p. 260—262°, has probably the formula $C_{11}H_6O_5$, and gives the anhydroacetyl compound

$$C_{11}H_2O_4(C_2H_3O)_2,$$

colourless, prismatic needles, m. p. 174—176°, whereas the latter, $C_{11}H_6O_5$, yellow needles melting above 300°, gives, with acetic anhydride, the compound $C_{11}H_2O_4(C_2H_3O)_2$, colourless, prismatic needles, m. p. 280—282°. It is probable that both compounds contain a carboxyl group.

193. "Note on the destructive distillation of ethyl gallate." By A. G. Perkin.

According to Schiff (*Annalen*, 1872, **163**, 217), on distillation, ethyl gallate gives pyrogallol and ethyl alcohol. This is so, but at the same time, towards the end of the operation, a considerable quantity of a red colouring matter sublimes, which has been identified as *rufigallic acid* (hexahydroxyanthraquinone) (found, C = 55·14; H = 2·63), by its acetyl derivative, $C_{14}H_2O_4(C_2H_3O)_6$ (found, C = 55·78; H = 3·85; $C_{14}H_8O_4$ = 55·09), m. p. 282—283° (not previously given), and by its dyeing properties. The yield was approximately 7 per cent., but considerable carbonisation occurs when this colouring matter is distilled. The reaction may be expressed as $2C_6H_3(OH)_3 \cdot CO_2Et = C_{14}H_8O_6 + 2EtOH$. Gallic acid itself, on distillation, yields a small quantity of the same substance (acetyl compound, C = 56·17; H = 3·77), whilst protocatechuic acid and its ethyl salt give a trace of a colouring matter resembling rufiopin. β-Resorcylic acid does not give rise in this way to any anthraquinone derivative.

194 "A series of double chromates." By S. H. C. Briggs.

The author has found that freshly precipitated copper hydroxide or carbonate dissolves in one equivalent of chromic acid to give a clear solution in the presence of twenty or thirty equivalents of copper sulphate, or ten to fifteen equivalents of copper silicofluoride, although in the absence of these salts the dichromate and a precipitate of basic salt are produced.

A double salt, $(NH_4)_2Ni(CrO_4)_2,6H_2O$, was obtained by adding ammonium chromate to a solution of a nickel salt. This could be recrystallised from water below 40°, although nickel chromate has never been obtained from aqueous solution, and ammonium chromate can only be recrystallised from solutions containing ammonia. Attempts to prepare the potassium nickel chromate and double chromates of ammonium and copper, zinc, cadmium, and manganese were unsuccessful.

By the action of ammonia on the mother liquors from the preparation of $(NH_4)_2Ni(CrO_4)_2,6H_2O$ from the chloride, a double salt, $(NH_4)_2Ni(CrO_4)_2,2NH_3$, was obtained, and corresponding copper, zinc, and cadmium compounds were formed by the action of ammonia on the dichromates. These double salts, on heating, lose water and ammonia, and undergo sudden decomposition between 200° and 300°, leaving a mixture of oxides.

ADDITIONS TO THE LIBRARY.

I. Donations.

Naylor, William. Trades waste: its treatment and utilisation with special reference to the prevention of rivers pollution. A hand-book for borough engineers, surveyors, architects, and analysts. Pp. xvi, 267, ill. London 1902. From the Author.

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Hall, A. D., and F. J. Plymen. S.E. Agricultural College, Wye. First Report to the Technical Education Committees of Kent and Surrey on a chemical and physical study of the soils of Kent and Surrey. Ashford 1902.

At the next ordinary meeting on **Wednesday, January 21st, 1903, at 5.30 p.m.**, the following papers will be communicated:

"Phenocycloheptene." By F. S. Kipping and A. E. Hunter.

"The absorption spectra of laudanine and laudanosine in relation to their chemical constitution." By J. J. Dobbie and A. Lauder.

"The relation between the absorption spectra and the chemical structure of corydaline, berberine, and other alkaloids." By J. J. Dobbie and A. Lauder.

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